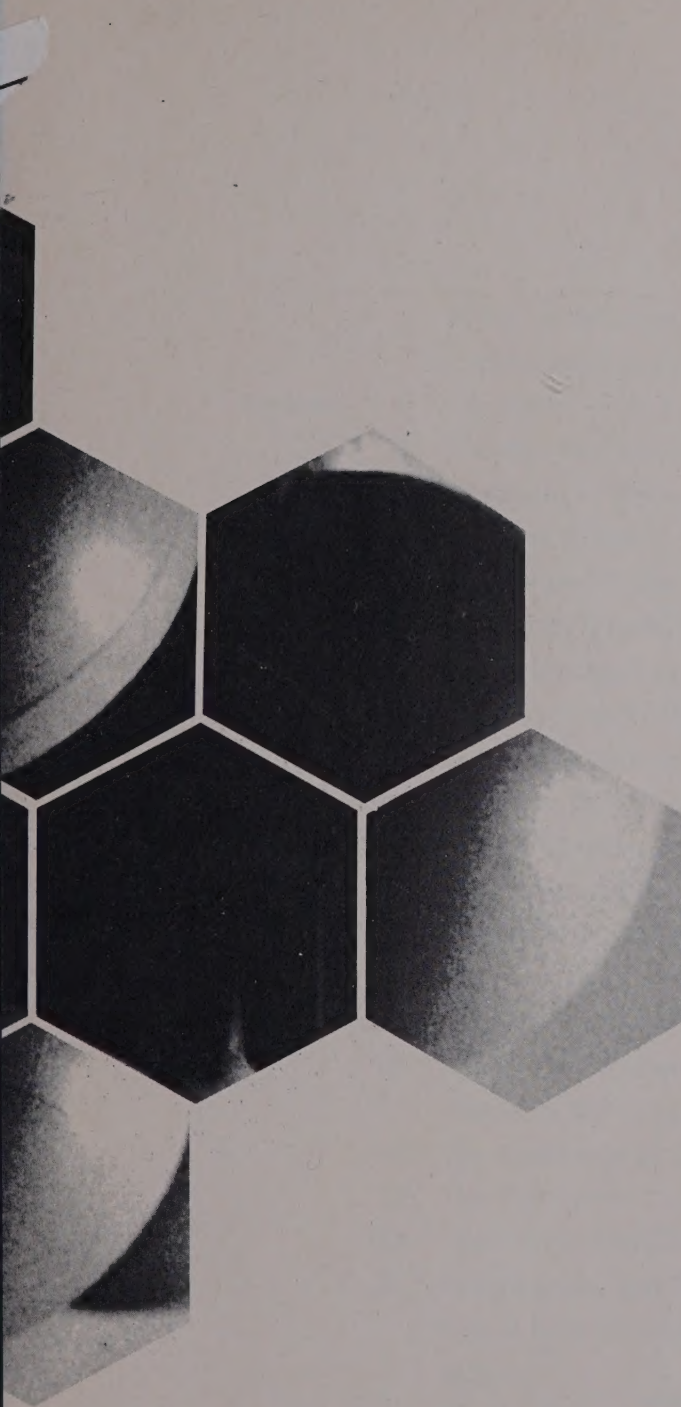


University Of Alberta



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TEACHER'S GUIDE

for Chemistry:
Experiments
and Principles

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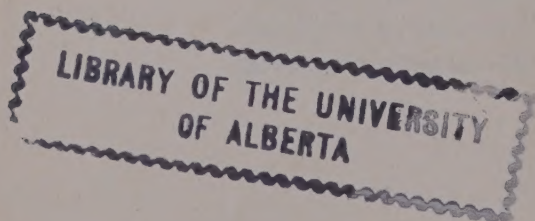
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Some Introductory Remarks

General Philosophy

Chemistry: Experiments and Principles follows the philosophy of the CHEM Study program from which it is derived. As the title indicates, experiments are used to introduce principles. Both are emphasized by repetition in discussion and in solving problems. Descriptive chemistry is not neglected, but it is used to strengthen the concepts under study rather than as an exercise in memory. Chemistry is learned as a science; facts are gathered and arranged in meaningful patterns which reveal regularities that lead to understanding nature.

Text Arrangement

The Textbook can be considered to consist of seven broad sections:

Introduction	(Chapter 1)
Atomic Theory and the Mole Concept	(Chapters 2-3)
Kinetic Theory	(Chapters 4-6)
Atomic Structure and Chemical Bonding	(Chapters 7-10)
Principles of Chemical Reactions	(Chapters 11-15)
Molecular Structure	(Chapters 16-18)
Application of Principles to Descriptive Chemistry	(Chapters 19-21)

There is considerable overlap among these sections. Fundamental concepts are introduced in the first section, developed in the second and third, and utilized in the fourth and fifth. The first three sections contain much descriptive chemistry, although this subject is not given major emphasis therein. The last two sections are devoted to descriptive chemistry, but the fundamental concepts are deliberately and pointedly used, again and again. This arrangement has significance for you as the teacher.

Exercises

These problems in the body of the Textbook are for the student to do when he comes to them during a reading assignment. They are designed to aid the pupil in checking whether he has understood the preceding material. Often the material immediately following assumes that the student has thought about the exercise.

Questions and Problems

The large supply of questions at the end of each chapter is classified by the chapter section to which they apply and their difficulty (see *Schedule* and *Related Material* for each chapter). Undoubtedly there are more problems than are needed except for accelerated classes. Probably one-half to two-thirds are appropriate for most classes, but you must judge the number and level suitable to your class.

The answers given in the Teacher's Guide are generally more complete than most students are likely to give, but they can serve as models for classroom discussion or provide information needed to satisfy the more demanding students. Hints are sometimes given to suggest errors into a constructive development of valid conclusions.

Vocabulary

Careful attention has been paid to the development and growth of the vocabulary. Technical terms are introduced deliberately, and, if not explicitly defined, they are juxtaposed with self-explanatory paraphrases. Sentences conveying conceptually difficult ideas are expressed as simply as possible. On the other hand, the growth of vocabulary is encouraged in sentences where the context easily defines the word and where a crucial message is not conveyed. In general, the reading level is Grade 11 according to the Flesch formula.

Laboratory Work

The treatment of laboratory work differs from that employed in many conventional courses. In this course, the student is often sent into the lab to investigate properties of nature before they are treated in class. He gathers some facts — that is, gets an experimental basis for understanding concepts — which the teacher then develops the next day. This technique is superior to sending the student into the lab to verify generalizations made by the Textbook or the teacher.

Most experiments should receive a short prelab discussion on problems of experimental technique and a postlab session devoted to the systematic development of relevant principles. The experiments are described for an ordinary scale of operations. A semimicro scale may be used by making certain obvious changes in a few experiments. Since a reduction in sample size might increase errors in weighing, careful consideration should be given to this possibility before reducing the scale of experiments which require weighing. A helpful reference is *Semimicro Experiments for the CHEM Study Program*, J. F. Schaff, K. H. Niedfeldt, and J. M. Brawders, D. C. Heath and Co., Boston, 1966.

Films and Demonstrations

Throughout the course, visual substitutes for actual laboratory work are used where appropriate. The Chem Study films are still suggested as an integral part of the course. The films cover material which the teacher would find very difficult or time-consuming to illustrate by the usual means. The demonstrations are described in detail, and the Textbook assumes they are done when indicated.

Achievement Tests

A series of exams has been prepared. Each set consists of 7 tests covering 2 or 3 chapters each, a semester final, and a year final. These are multiple-choice, open-book tests designed to measure whether the student is mastering the course content, that is, whether he understands the major principles well enough to apply them to new or parallel situations. The tests may be ordered from D. C. Heath and Co., 285 Columbus Avenue, Boston, Mass. 02116.

Extra Information

The Appendices (in Textbook and Laboratory Manual) contain quite a bit of extra information. Remind the students of this occasionally. In addition, the index is a handy guide to all the information in the Textbook. Encourage the use of these aids by letting students see that you use them often.

Organization of the Teacher's Guide

Each chapter has a guide which follows the outline below. In the outline is a short statement of what is to be found in each section.

The first four items provide a quick panorama of the chapter, and could be considered a very short form of guide. The sections headed *Development* and *Answers to Exercises and Problems* give detailed support for the specific textual material. The *Background Discussion* makes available a treatment of the important chemical principles and scientific philosophy. This section is intended to help you give added depth to your presentation, but is not intended directly for the student.

In addition there is an index of the Teacher's Guide for locating specific information and a list of supplies needed.

Intent and Approach

About one page, discussing the overall philosophy of the chapter.

Outline

Quite brief, with section numbers used to relate ideas to the Textbook.

New Concepts

A short list (5–10 items) of *major* new concepts — the things a student should learn from the chapter.

Schedule and Related Material

A suggested order of class, laboratory, and film presentations. The relation of exercises and problems to Textbook sections is shown along with an indication of problem difficulty.

Development

A section-by-section discussion of the Textbook. Included are typical questions and ideas about how to handle each concept with additional examples and suggestions. Each Experiment and Demonstration is described in the *Laboratory Guide*. See the introduction in that guide for the organization used.

Supplementary Material

Listing of films, monographs, articles, and books for student reading and teacher reference. Brief descriptions are often included. A list of film sources is included at the back of this book.

Background Discussion

Material on chemical principles and scientific philosophy for teacher's benefit. Only incidentally would it appear in the classroom.

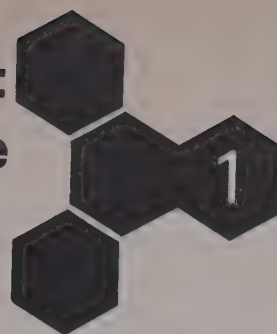
Answers to Exercises and Problems

Exercises and problems are given with full answers. A hoped-for student answer is given, often with an extensive discussion.

Suggested Quiz Questions

More than enough questions for one quiz are given — with answers. The questions are designed for open-book use. Questions are supplied for Chapters 1–17. Since teachers differ in their interests, they may treat the remaining chapters in different ways. Accordingly, chapter tests are not included.

Chemistry: An Experimental Science



1

Intent and Approach

In the first chapter we treat science as a human activity. We do more than just describe the activities of science; we also hope to give the student a sense of the significance of these activities. For many students, this course may be their first educational experience that deliberately goes beyond: "What are the facts accepted by authority?" and "How are these facts rationalized with other knowledge (that is, how are they explained)?" Perhaps for the first time the student will consider the questions: "Where do the 'facts' come from?" and "What does it *mean* to 'explain' facts?" The answers to the last two questions constitute the message of this chapter, the most abstract message of the course.

Answering such questions requires introspection—a difficult process for most of us. Yet the ideas in this chapter are probably the most important in the book. This is true both for the science-bound and the science-terminal student. Both types of students need a correct view of the underlying pattern of science and of the meaning, limitations, and purposes of this pattern.

Since the message of this chapter is important and because it is abstract, it has been carefully stated in simple language and couched in familiar metaphor. It has been stripped of the formal trappings that are characteristic of a highly organized system. Thereby the fundamental ideas are placed in sharp focus.

Outline

The activities of science (1-1) are brought up in a general discussion.

Observation and description (1-2) emphasize the important first step of scientific method. Experiments 1 and 2 provide the laboratory experience.

The search for regularities (1-3) introduces an activity that may be new to the student. It is so basic to understanding the method that it is illustrated first by a nontechnical example: the "lost child" analogy. Next is a chemical example dealing with properties of gases (1-4) and, in particular, the relation between pressure and

volume (1-5).

A section on wondering why (1-6) starts in a general way and then leads into the particle model of gases. The use of well-understood analogies to answer "why" questions is developed.

The ways to communicate are illustrated in terms of words, equations, and graphs applied to $PV = \text{a constant}$ (1-7).

Uncertainty flows from the apparatus and technique used (1-8) and from the ways in which the data are combined (1-9). A review section (1-10) repeats the main steps: observe, find regularities, wonder why, communicate.

New Concepts

1. The scientific approach to problems.
2. Explanations and models.
3. Uncertainty in measurement.
4. $P \times V = \text{a constant, at fixed } T$.
5. The presence of subunits—atoms—in the molecules of gas.

Schedule and Related Material

This table is to give you a quick view of the interrelation of the laboratory work, films, problems, and class discussion. The various sections of the text are listed with experiments, demonstrations, and films interpolated at the optimum places. The time required for each experiment is given in the Laboratory Guide. You must decide timing on the class work and add tests as needed. The suggested time just above the table is only

a rough guide. The total of all these times is 183 days for the 21 chapters.

When experiments are listed between sections, as Experiment 2 before Section 1-3, then that order should be followed to preserve the proper sequence of the student observing first, finding the regularity next, and so on. The relevance of exercises and problems is given and an estimation of problem difficulty included.

SCHEDULE AND RELATED MATERIAL

Suggested Time: 10 days

Text Section	Topic and Other Work	Exercises	Problems		
			Easy	Medium	Hard
1-1	Expt. 1. Observe Candle				
1-2	Activities of Science				
	Observation		1-3		
	Expt. 2. Observe Reaction				
1-3	Regularities		4, 6	5	
	Expt. 3. Density				
1-4	Gases	1	7, 8		
1-5	Pressure—Volume		13-16, 19	12	
	Demo. 1. Pressure				
1-6	Wondering Why		17, 18		
1-7	Communication	2		20	21
	Expt. 4. Buoyancy				
1-8	Uncertainty		22, 23	9*, 10*	11*
1-9	Derived Uncertainty	3, 4			
1-10	Review				

* Must follow Expt. 4.

Development

Introduction

Before the first day of class, it is important to realize that some of the initial procedures recommended may differ from your normal method of operation. Teachers ordinarily develop routines for the first day or two of school, involving such activities as checking out textbooks, assigning seats, checking out lockers, and other bookkeeping chores. You are asked to postpone as much of this as possible and, on the first day, after a few introductory remarks, to send the student to the lab to begin his own observations. He should return to the lab soon afterward to observe a chemical reaction (Experiment 2) and a regularity (Experiment 3). A reaction to this procedure might be, as it was for a number of the teachers who tried it, that, "Yes, this looks good on paper, but it will not work in my situation." If this is your reaction, then be reassured by the fact that these teachers *did* try it and were convinced that it *did* work and that they had never before experienced such a successful beginning to a course.

The work of the first chapter and the related experiments are intended to give the student a feeling for the "activities of science." He is to be made aware that science is based upon observation; that observation must necessarily contain uncertainty; that from observations a search is made for regularities; and that from the regularities arises the third basic activity of science—"wondering why."

The schedule to be followed has been arranged to insure that these concepts become part of the student's experience in an orderly sequence. He begins with his own observation of a burning candle and a reaction. Next he finds a regularity from experimental data. Having engaged in these very activities, he can relate the formal discussion directly to his own experiences. These early trials at measurement also prepare him to understand the source of uncertainty in measurements.

Expt. 1, SCIENTIFIC OBSERVATION AND DESCRIPTION,

fits here. See p. 2 in the Laboratory Guide.

1-1 The Activities of Science

The fundamental steps of the scientific approach are discussed. The student should be brought to feel that this is a powerful way to get knowledge. In fact, most of them already know the method. Any detective story follows the pattern. It is used by the boy learning what is wrong with a car by making observations. In the same way, a young lady follows the actions of her friends to learn about them. In a science course, perhaps more formal emphasis is put on the method, but it is not really a new concept. The biggest gain is that the student becomes conscious of the method, and his use of it is made systematic.

1-2 Observation and Description

Most beginners do not really *observe* what they are looking at. Experiment 1 helps show this lack and the wealth of things to see even in a common object. You will have to work on the matter of description. Most young people find expression of their thoughts difficult. Some guidance in the way to report experimental results is also needed. The main defect is lack of straightforward organization. Another major mistake at first is giving conclusions instead of observations.

Expt. 2, OBSERVING EVIDENCE OF INTERACTION,

fits here. See p. 4 in the Laboratory Guide.

1-3 The Search for Regularities

After a scientist has made a series of observations,

his next task is to consider: "What regularities appear." Stress that, once regularities have been found, a number of observations can be classed together and used more effectively.

Some of your students may regard the analogy of the "lost child" as too elementary, yet it actually conveys the most sophisticated idea of the course. Observe that this simple example encompasses all of the activities in which scientists are engaged. All of the painstaking years of experimental study, all of the involved mathematical analyses, can be understood in terms of the actions of this child in observing, seeking regularities, generalizing, and testing his generalization.

Emphasize that a generalization is reliable within the bounds defined by the observations and that it may or may not apply beyond these limits. Further, point out that the generalization *must* come after the experiment. The scientist must have data among which to seek a regularity. As a direct example of a search for regularity, develop the generalization concerning density found in Experiment 3.

Expt. 3, SEARCHING FOR A REGULARITY,
fits here. See p. 6 in the Laboratory Guide.

1-4 Some Properties of Gases

Throughout these pages your aim should be to give simple data to convince the student that the gas particles are different. Solubility in water, gas color, and reactions with litmus and oxygen are all used to supply this data. Some simple demonstrations of these will be seen in the film on gases. Keep in mind that the student is not ready for any reactions or other "explanations" of what occurs. Lead him to see that different properties of the samples imply different kinds of particles, which are called molecules.

The gases used fit with the film on combining volumes in Chapter 2. Also they occur in the first equation the student will see (Chapter 2), and the example used to introduce equilibrium (Chapter 13). Do not change these for other gases which will not be exploited later.

1-5 Measurement of Gas Pressure

The pressure of a gas is discussed here in terms of its measurement and later in terms of its cause. You can best develop this section by showing a mercury barometer and by using a curved glass tube, sealed at one end (see Figure 1-5, Textbook, p. 7). This type is called a **J-tube** apparatus in the catalogs of some scientific instrument companies. The Torricellian barometer can be effectively demonstrated (see Figure 1-4, Textbook, p. 6) as follows. Take a heavy-walled glass tube, which must be 31 inches or longer, and fill it with mercury. Carefully invert the tube into a beaker of mercury. Some of the mercury will run out of the glass tube until the pressure of the mercury column balances the atmospheric pressure.

Questions frequently arise at this point in connection with the diameter of the tube, the use of a liquid other than mercury, the surface area of the exposed mercury in the beaker, and so on. Elementary physics texts review these principles. Briefly, the height of the liquid in the tube depends upon the liquid density and is independent of tube diameter or the surface area of exposed liquid in the beaker. Remember that the pressure is measured in terms of force per unit area. By demonstrating this with tubes of several diameters, it can easily be shown that the height *is* the same in each tube. The Laboratory Guide (p. 11) describes construction and use of a device to illustrate this point.

Demo. 1, PRESSURE,

fits here. See p. 11 in the Laboratory Guide.

In demonstrations utilizing the curved tube, the relationships become more meaningful when students perform the actual measurements, record the data, and then graph the change in volume with respect to pressure. You can have some students take readings, others record data at the chalkboard, and still others plot data on a graph at the chalkboard.

1-6 Wondering Why

This activity is explained as the search for a model system that can be used to explain an observed regularity. The model system is framed in terms of a process that *is* well understood and is used to explain a process *not* well understood.

The example, which relates the behavior of steel balls in a plastic box to the behavior of a gas, is used to indicate what constitutes a "good" explanation. That is, the model system chosen must be well understood, and there must be many and close similarities to the system being studied. Some students may object that we had to keep shaking the box to maintain the balls in the "gas phase" while the real gas particles do not require shaking. You can remind them that the real gas has perfectly elastic collisions while the steel balls do not. The shaking is to overcome that lack. Don't try for too much explanation here as the student doesn't yet know much about energy or phase changes.

It is often helpful to remind the student that models for unknowns are not new to him. They are a common item in conversation. Ask a sports fan or a high school coach, "How do you play rugby?" He will probably answer, "It's like football." The answer suggests a *model*—a well-known example which has certain similarities to the unknown one. The next part of the explanation about rugby might very well be "But you are not allowed to block or run ahead of the ball carrier." The difference between model and unknown is explored. We did this same thing in the gas model. We specified "small," or even "tiny," balls.

The next step in deriving implications is less frequently heard in everyday usage. But let us pursue the rugby-football example. The person hearing that no player can run ahead of the ball carrier nor block for him might think a moment and then say: "Well, there must not be a forward pass play (correct), and the runner must have a rough time of it (not necessarily)." The last, partially wrong, implication does not allow for the lateral or backward pass—a very common play in rugby.

As another example, suppose a music teacher

is asked "How do you play a harp?" The first response might be, "It's like a piano (setting up the known as a model), but the strings are plucked instead of struck by hammers (differences are brought out)." The answer shows that the teacher expects to make use of the student's background in reading music, understanding chording, and so on.

Bring out and emphasize that a model permits predictions, which may or may not be correct, *and* that there is a real difference between model and system—rugby is *not* football; a harp is *not* a piano; the moving billiard balls are *not* gas molecules. Notice that care is taken to avoid the words "molecule" and "atom" until these terms are logically needed in this section. There is distinct pedagogic advantage in waiting till the student sees the need for the word and gets a clear, operational picture of why atoms are needed (as subunits of molecules).

1-7 Communicating Scientific Information

A scientific advance is important only if it is communicated to others. Because of this, the proper choice of terms and use of language are of prime importance.

When a regularity is found, there are several ways by which it might be reported. The choice of methods depends on the set of observations and on the use to which it is put. It can be expressed as a qualitative statement, as a table of data, as a graph, or as a mathematical relationship.

Note that the example $PV = a \text{ constant}$ is *not* a signal to start developing the gas laws. Postpone that topic until Chapter 4. The equation appears here only as an example of a way in which a regularity can be expressed. It is deliberately chosen in order that the same example can be used to introduce the formation and molecular motion of liquids. In addition, its use here helps with the gas laws in Chapter 4.

Expt. 4, WEIGHING AN OBJECT IMMERSSED IN TWO DIFFERENT FLUIDS,

fits here. See p. 12 in the Laboratory Guide.

1-8 Uncertainty in Science

A scientific statement of a measured quantity is well framed if it clearly conveys just what is known and nothing more or less. To illustrate this, ask the student to consider his own measurement of mass (Experiment 3). Also he might think about the limitation inherent in his ability to read a thermometer precisely. Many other examples can be used, such as measuring distance, volume, and so on.

Note the connection between the apparatus used and the uncertainty brought out in Figure 1-11, Textbook p. 13. All three of the reports listed are "good" measurements when "good" is matched with the purpose for the data. Beginning experimenters often make one measurement very precisely but fail to do other portions with equal care.

Some typical values for common measurements are given in Appendix 7 of the Laboratory Manual and are repeated here in Table 1-1.

Make constant and consistent use of this idea in order that the student will feel it is important but not mysterious. The experiments provide a chance to check the understanding achieved by the class.

1-9 Uncertainty in a Derived Quantity

This section serves two purposes: (1) to illustrate how to express the uncertainty in a derived num-

ber and impress the student with the need for such expression and (2) to give some help with the calculations required in later experiments. The first is the one to stress. Throughout the course you should show your awareness of the uncertainty in measured and derived quantities.

When he has completed this chapter, the average student should know how to determine uncertainty if only sums and differences are involved. By the end of the first semester, most students should be able to determine uncertainty when products and quotients are involved. The calculation of average deviation from the average will be understood by the better student if you perform this operation for the results from several experiments.

TABLE 1-1

Uncertainty Found with Typical Laboratory Instruments

Typical Instruments	Typical Uncertainty
Triple-beam (centigram) balance	± 0.01 g
Platform balance	± 0.5 g
50 ml graduated cylinder	± 0.2 ml
10 ml graduated cylinder	± 0.1 ml
-20°C to 150°C thermometer	$\pm 0.2^{\circ}\text{C}$
50 ml buret	± 0.02 ml
50 ml gas-measuring tube	± 0.02 ml

Supplementary Material

Books

1. THE CHEMICAL HISTORY OF A CANDLE, M. Faraday, Viking, New York, 1960.
This pocket book reproduces Faraday's famous series of "Christmas lectures" on the candle. It is suitable for all students.
2. EXPERIMENTATION AND MEASUREMENT, W. J. Youden, National Science Teachers Association, Scholastic Book Services, *Vistas of Science* 2, New York, 1962.
A simple explanation of the treatment of data through the use of examples from student experiments. Valuable for the teacher and for any student interested in the subject. Not highly mathematical.

Programmed Sequences

There are two skills that are very helpful to students of science. These skills are not properly part of chemistry, hence we do not recommend they be taught in this course; but since they often give trouble, some help is available for the student needing it.

These skills are expressing and manipulating numbers using powers of ten and using a slide rule. The first is used in the Textbook, and some explanation is given, along with a few exercises,

in Laboratory Manual Appendix 6. The use of a slide rule does not come up explicitly, but of course it is a great help in doing the problems.

There are some programmed sequences to help the *student teach himself* these topics. This technique (which you may have heard described as “machine teaching”—though the sequences require no machines) uses a series of questions, each a very small extension of the student’s knowledge. After answering, the pupil checks the correct answer in the right margin and then moves to the next item. In theory, the quick affirmation of his answer (usually correct because of the small “steps”) raises his confidence and reinforces his learning.

The intended procedure is that you determine by observation which students need help, then lend them the appropriate sequence for home study. Since the sequences themselves are not marked by the students, they can be reused as

required. The sequences are :

Use of Exponential Notation

- Powers of ten and exponential notation of numbers
- Shifting the decimal point
- Multiplication and division
- Extraction of square roots
- Addition and subtraction

Use of the Slide Rule

- Reading the scales
- Multiplication
- Division
- Extraction of square roots

These programmed sequences may be ordered from W. H. Freeman and Co., 660 Market Street, San Francisco, California, 94104. One copy of *Exponential Notation* is 40¢, *The Slide Rule* 25¢; both together 50¢.

Background Discussion

The Essence of Science

This chapter is designed to establish the essence of science in the student’s mind. In spite of all your efforts some students may give this chapter only superficial consideration, regarding it as too elementary. Any student who feels this chapter is too elementary has missed its message. His interest can probably be awakened by asking him such questions as the following :

1. According to Chapter 1, why is man curious? Why are you curious?
2. According to Chapter 1, an explanation reveals a hidden likeness to something already known. Can you think of explanations where this hidden likeness can be pointed out? Can you think of explanations where this definition of an explanation is not correct?
3. Some philosophers believe in the existence of scientific ideas that are surely true without the slightest bit of supporting evidence. Chapter 1 indicates that *every* statement of regularity is a paraphrase of experimental facts. Can you

think of any scientific idea that you believe can be shown to be true without using any experimental facts? (Eliminate, without discussion, any proposal of a religious flavor.)

4. Can you think of a more sophisticated fable?

The Fable

Science actually moves forward in exactly the way the child developed his regularities regarding combustion. The fable contains some important notions set in a transparent example, in order that the reader can see every false step as it occurs. If a student feels the example is too elementary, ask him to think of a more sophisticated fable, and then examine his offering for the following ideas.

1. A theory, law, or regularity need not be correct in every context to be useful in a limited context. (For example, in the woods, the rule “cylindrical objects burn” would be useful, since few nonflammable cylindrical objects are found in the woods.)
2. There is no assurance that a regularity found

within a certain range of experience applies outside of this experience.

3. Implications of a regularity (predictions) lead to experiments outside the range of experience upon which the regularity was based.
4. Laws in agreement with presently known information may, nevertheless, be changed or abandoned in the future as additional experiments increase our knowledge.

Stress the idea that scientific advance does *not* involve a special process that is incomprehensible to most people. Though some people are better at the game than others, the process is understandable to all. Avoid giving science an air of mysticism through historical eulogies that emphasize the "stroke-of-genius" cliché. Instead, make it clear that the recognized genius is merely better at actions that we all can do. Imply that "Everyone can apply scientific method; you may have to work a little harder, but why not try?"

Finally, stress that science is constantly changing as our knowledge increases. Science is not a completed structure but a growing one. Let the student see how exciting the future of science is to you, the teacher; make him aware that he can contribute to this future.

Regularities: Rule, Law, Theory

The simple skeleton of scientific activity—observe; find regularity; find explanations (hidden regularities)—could be elaborated at great length. Don't do this. Avoid encumbering this simple view. Let the student begin his study of science confident that he will understand what he is doing.

To give an example, no semantic distinction is offered between a rule, a law, and a theory. They are all presented as expressions of regularity. Useful argument can be made in favor of a semantic distinction. The more abstract expressions of regularity are usually called "theories."

However, the likenesses among these statements of regularity are more important to an understanding of science than are their differences. Compare the *Law* of Conservation of Energy and the *Atomic Theory*. Why is one a law and the other a theory? Energy is a derived

quantity, not a measured one. Temperature is measured, not heat. Velocity and mass are measured, not kinetic energy. Chemical energy is *never* measured—its existence is implied by the model that states that if heat is expended in bringing on a chemical change, some other, unseen form of energy must have been stored. In beta decay, energy is indeed lost, but we "saved" the Law of Conservation of Energy by inventing an undetected particle, the neutrino. Thus the Law of Conservation of Energy is a model. It has great value because it aids us in correlating a wide variety of measurements: position, velocity, temperature, voltage, current, chemical composition. This is just the language we would apply to the Atomic Theory. It, too, is a model. It, too, has great value because it aids us in correlating a wide variety of measurements: *PVT* measurements, composition of substances, mass relations in reactions, crystal structures. We see that there is great likeness here.

In a real sense, even laws which seem to relate directly to measurements are models. Consider Boyle's Law. The rule $PV = a \text{ constant}$ doesn't really fit any gas perfectly. Deviations from this behavior are small but measurable at normal conditions. At higher pressures, the deviations become large. Near its critical conditions, a gas doesn't follow Boyle's Law at all. Neither NO_2 nor H_2O follows the law even under normal conditions (we "explain" this by saying that association occurs). The law $PV = a \text{ constant}$ really applies, then, to a model gas (an "ideal" gas). This model has great value, because it aids us in correlating pressure-volume measurements on many real gases over a wide temperature range.

We see that these laws and theories have a common function: they correlate results of measurements and, in so doing, aid us in dealing with the knowledge given us by these measurements. If the student comprehends the nature of this common function, he will have no difficulty realizing for himself that this correlation can be carried out at different levels of abstraction.

Chemistry Undefined

You may be surprised that this first chapter has

no definition of chemistry.

How do other authors define chemistry? They usually begin with words of caution about the danger of trying to convey the scope of chemistry in a definition. Then the definition may be offered that chemistry is the science concerned with structure, properties, reactions, and energy effects associated with substances. There are two quite different problems raised by this definition. The first is that some of the words in the definition are rather meaningless to a person who has studied no chemistry (for example, consider the word *substance*). Why give the definition at this time if it is unintelligible? The second problem is that the definition can be construed to include all of science.

Mature scientists can do better in defining chemistry because they have more vocabulary to aid them. Since we accept the nuclear atom, we can see that a chemist is generally concerned with the behavior of matter associated with the electrons surrounding the nucleus. He is, furthermore, generally concerned with relatively pure substances. With this general background, he may attack any problem on which he can make progress. These problems, then, become part of chemistry.

For example, as chemical knowledge has increased, it has become possible to apply standard methods of chemistry to biological systems. There is no longer any question that the same principles that govern all chemical systems are operative in living systems. A substantial part of biology is now taken to be chemistry; it is called biochemistry. Another example is provided by nuclear chemistry. The determination of the fate of a nucleus on bombardment or decay is frequently a problem requiring a deep knowledge of chemistry. This being so, chemists are better equipped to solve some problems concerned with the structure of the nucleus than are physicists. Hence a substantial part of nuclear physics is now within the purview of chemists.

Thus chemistry is "what chemists do," and it is a changing thing. What is outside of today's definition of chemistry may be within chemistry by the time today's student is a practicing chemist.

Experiment and Theory

All scientific knowledge is based upon our knowledge of the environment as derived from experimental observations. Hence this course places great emphasis on the experimental aspects of chemistry. A valid picture of chemistry must include direct laboratory experience. Furthermore, this laboratory work must be carefully integrated into the course to show the relationship between laboratory results and the increased understanding that stems from them. There is distinct loss if the timing of experimental work is governed by the expediency of laboratory availability. The timing should aim to furnish the student with *prior*, relevant experience that he can bring to mind when a given principle is presented. He must be given the opportunity to experiment without having a firm expectation of the outcome; he should have the opportunity to discover principles himself, through his own laboratory work. Through prior participation in appropriate experiments, a student will fully realize how principles are derived and why they are retained. For these reasons the student is placed in the laboratory on the first day of the course.

Prediction

One of the most appealing rewards of scientific activity is the development of predictive power. Let us examine the various kinds we can attempt: repetition, interpolation, and extrapolation.

Repetition of an experiment is expected to yield the same result obtained earlier. Consequently, repetitious experiments offer the most elementary opportunity for prediction. In fact, science is built upon the assumption (and the corroborating experience) that a scientist can predict with confidence the result of an experiment that duplicates an earlier set of operations. If the important conditions are known and properly controlled, then this result should be close to the earlier result. If a large difference is found, then some important (but perhaps unknown) condition is not being allowed for. As the experiment is repeated many times, the likelihood decreases that such an important condition will go undiscovered.

Interpolation is a higher form of prediction. A succession of two or more experiments in which one condition is varied systematically provides a basis for interpolation within the range of the variation. There always remains a possibility that an unsuspected behavior occurs at intermediate values of the variable condition. The likelihood that this will happen decreases as we increase the number of measurements used to establish the trend. Of course the same limitations mentioned for repetitious experiments apply here, too. The probability of a surprise decreases as the explanation of the trend gains support by fitting a wider range of data.

Extrapolation represents the true realm of prediction. What can a scientist predict with confidence that is outside his range of experience? The term "with confidence" is the key expression here. The answer is that the further he goes beyond his range of experience, the less confidence he can enjoy. The confidence that an extrapolation deserves is fixed by the weight of the experimental support for the basis of extrapolation and by the distance of the extrapolation. This is true whether one is predicting the PV behavior of ammonia at high pressure from measurements made at lower pressures or predicting a quantum-mechanical result for the nucleus on the assumption that quantum mechanics holds for nuclei because it holds for atoms. A theory which is used for prediction without *any* experimental basis deserves no confidence whatsoever.

Examples are legion. Consider Table 1-2, which shows the PV behavior of a mole of ammonia between 0.1000 and 0.6000 atmosphere. The regularity $PV = 22.37 \pm 0.05$ permits one kind of prediction: interpolation over the range 0.1–0.6 atmosphere pressure with uncertainty near ± 0.05 , or 0.25%. It also provides a basis for extrapolation: at 1.000 atmosphere, the volume is expected to be $22.37/1.000 = 22.37$ liters; at 2.000 atmospheres, it is expected to be 11.18 liters; at 4.000 atmospheres, it is expected to be 5.592 liters, and at 5.000 atmospheres, it is expected to be 4.474 liters. Do all of these expectations deserve the same confidence? By no means. The further we depart from the area of our ex-

perience, the less confidence we can enjoy. To show that this is so, consider Table 1-3 which

TABLE 1-2

PV Behavior of 17.0 g of Ammonia Between 0.1000 and 0.6000 Atmosphere at 0°C

P (atm)	V (liters)	PV
0.1000	224.4	22.44
0.2000	111.6	22.32
0.4000	56.02	22.41
0.6000	37.20	22.32
Average		22.37 ± 0.05

TABLE 1-3

Contrast of Extrapolations (from Table 1-2) with Experimental Values for 17.0 g Ammonia at 0°C.

P (atm)	V_{calc} (from $PV = 22.37$)	V_{expt}	% Error in Prediction
1.000	22.37	22.264	0.5
2.000	11.18	11.051	1.2
4.000	5.592	5.4520	2.6
5.000	4.474	0.02	catastrophically large

contrasts our extrapolated expectations with very accurate experimental results. The experiments up to 4.000 atmospheres do show a growing deviation from our expectations. In retrospect, all we can say is that we should not feel chagrin that this is so—after all, we made an excursion from the range in which $PV = 22.37 \pm 0.05$ is known to hold. Outside this range of experience we were relying upon hope alone. But, more important, observe what happened to the prediction at 5 atmospheres! There is no connection at all between the expected volume, based on $PV = 22.37 \pm 0.05$, and the actual volume of the liquid that has formed. From gas measurements alone, this behavior could not be anticipated. Furthermore, the ornate model that

explains so well the behavior of gases (the kinetic theory) provides no basis for expecting the discontinuity of behavior. In fact, the model gives us a false confidence in extrapolation.

There are many such familiar examples—behaviors observed so often before that we are no longer surprised by them. For example, if asked to extrapolate the density of a newly discovered solid substance to a temperature above the explored range, you would undoubtedly qualify your answer by saying “provided it hasn’t melted already.” You are used to this discontinuity in the behavior of a solid. Would you have the same doubts about extrapolating this *downward* in temperature? You should have. Many solids change crystal forms as temperature is lowered. Electrical conductivities of metals provide an even more dramatic example. High-temperature measurements of electrical conductivities give no basis whatsoever for expecting the complete and sudden loss of all resistance by the superconducting metals. One of the most advertised erroneous extrapolations was the assumption that the classical laws of physics held on the molecular level. Progress in elucidating the behavior of matter on the atomic level had to await Bohr’s courage in recognizing that extrapolating classical physics to objects of atomic dimensions need not be correct.

Despite all this, we are continually hearing of successful predictions by theory. These do occur, and they represent the “special reward” we have associated with the discovery of a “hidden likeness.” With the aid of a model, it may become apparent that two types of behavior imply a third type. Then we may say that we can predict the third type. In a real sense, however, we see that the model (or theory) has aided us in interpolating—that is, in filling in as yet unexplored areas which are within the bounds implied by previous experiments.

An elementary example would be the prediction of PT behavior of a gas from a study of the PV and VT behavior. A more abstract example would be the prediction of acoustic properties of a gas from the kinetic theory established on the basis of observed PVT behavior of a gas.

How Theory Leads to Experiment

The foregoing discussion is concerned with the limited ability of a theory to predict outside of the area in which it is known to agree with experiment. It should not, however, becloud the value of a well-substantiated theory. Several times in the Textbook the student is reminded that science could not advance if our overwhelming mass of knowledge were not ordered with the aid of theories. Our power in dealing with the environment must be attributed to the principles that give coherence to different types of information.

His ability to recognize and to use the operative principles distinguishes the scientist from the inventor. An inventor is a person who proceeds on an empirical basis, relying mainly on his own experience. A scientist, on the other hand, proceeds in his search for and application of new knowledge with cognizance of the broad generalizations of the fundamental principles of science. In so doing, he brings to his own use all of the accumulated knowledge that lies behind these principles. In effect, he multiplies his own ability by the number of scientists who have preceded him.

Thus the scientist is continually guided and aided by his theories. As a result, he avoids conducting fruitless experiments; instead he proceeds quickly to crucial experiments extending beyond the firm expectations that can be based on earlier studies.

The Evaluation of Data

To evaluate and interpret data in an intelligent way, a student must have a clear understanding of uncertainty in measurements. He must realize that measurements are never exact. The reliability of data is fixed by the nature of the equipment used, the method, and the skill of the experimenter. Under any set of conditions, though, there is some limit beyond which finer measurements cannot be made.

At the start of your discussion of data, it is a good idea to distinguish between two terms which are used in science with a clear-cut differentiation—precision and accuracy. Precision refers to the

extent that a measurement deviates from the average of many measurements; it measures reproducibility. Accuracy refers to the extent that a measurement agrees with a true, known value. These two terms have familiar counterparts in educational testing: reliability and validity. The degree to which a set of test questions correlate with each other in identifying a group of students (for example, according to ability, achievement, and so on), measures the reliability of the test. This is a matter that can be clarified by rather straightforward statistical methods. It is quite another matter to determine whether the test actually measures the desired characteristic. That is, it is difficult to determine the validity.

In the same way, an experimental technique designed to furnish, say, the molar mass of a gas will have some precision limitations fixed by the actual manipulations required. These precision limitations determine the degree to which successive measurements reproduce each other. As is true of test reliability, such limitations can be estimated readily by performing a sufficient number of experiments. Furthermore, the effect on the uncertainty can be reduced by improving technique and, usually, by averaging the results of many experiments. In addition, however, there remains the quite separate question of whether the method, whatever its reproducibility, measures the quantity actually desired (in this example, the molar mass). Thus, if a gas density measurement is made, it may be quite reproducible if conditions are carefully controlled, but if the gas is not a perfect gas, Avogadro's Hypothesis is not perfectly applicable! Then there is an inherent error in the method, and this error fixes the *accuracy* of the measurement.

For this example (a gas density molar mass) experience with many gases furnishes a basis for estimating the extent to which gas imperfections are liable to cause deviations from Avogadro's Hypothesis. Most gases under normal conditions are in accord with Avogadro's Hypothesis within 1%. Hence any given molar mass determination must be assigned an uncertainty of about 1% because of *accuracy* uncertainty. In addition, there is an uncertainty due

to reproducibility that depends upon the balance used, the accuracy of the volume measurement, the technique of flushing the container, and other experimental details. If several successive measurements fluctuate about 5% above and below the average, then the principal uncertainty arises from precision limitations. If, however, all of the operations are so much improved that the reproducibility uncertainty has been reduced to 0.1%, then the principal uncertainty must be due to the accuracy limitation arising from the assumption made regarding Avogadro's Hypothesis.

In general, the types of errors that arise from measurements can be segregated into two groups: those that affect precision and those that affect accuracy. The errors that affect precision are called *random* or *indeterminate errors*. These errors are due to poor equipment and to carelessness in making proper observations. They as often give a result that is too high as they do one that is too low. From the nature of these errors, it should be clear how they can be minimized: by greater care, by experience and practice, by improved apparatus, and so on. The errors that limit accuracy are called *systematic* or *determinate errors*. This type of error always affects the measurement in the same way, no matter how many times the measurement is made. Thus the error is reproduced with each determination. For example, if the zero-degree position on a thermometer is marked incorrectly, the use of this thermometer would introduce a reproducible error. The results obtained in a determination involving the use of such a thermometer could be extremely precise but not very accurate.

Repeating a measurement many times reveals the magnitude of the random errors. The average of many measurements tends to eliminate uncertainty due to random errors. On the other hand, repetitions of the same measurement neither reveal nor remove uncertainty caused by systematic errors. Only changes of the method of measurement will provide a clue to the probable accuracy. *A measurement with high precision does not necessarily have high accuracy.*

Usually reproducibility is measured, and as a result the uncertainty associated with precision

BACKGROUND DISCUSSION

can be stated. The uncertainty due to accuracy is less readily learned and is often unknown. In such a case, the uncertainty due to reproducibility is used to estimate the uncertainty quoted, *and it is identified as the precision*. Thus a molar mass measurement might be stated to be 101 ± 3 , accompanied by the explanation that "the results have a precision of 3%." The $\pm$ factor can be calculated as the average deviation from the average (as done in Exercise 1-2) or as the standard deviation. Each of these clearly indicates that the uncertainty quoted is that associated with reproducibility. *It should not be inferred that doubt about the accuracy contributes nothing to uncertainty just because it is not mentioned.*

Section 1-9 in this chapter shows how to express uncertainty using significant figures or the symbol ($\pm$). Significant figures must be used with attention to the limitations listed hereafter. Students will have difficulties with the propagation of uncertainty through algebraic operations. Don't expect too much—instead, build their understanding through your repeated use of uncertainty calculations during the semester. Frequently remind the student of the meaning of significant figures—the number of significant figures shows all the digits that are certainly fixed by the numbers that were combined plus one more digit that is uncertain.

The Advantages and Disadvantages of Significant Figures

There are real advantages to the development of good habits in reference to uncertainty. We have adopted a simplified procedure. It combines some of the ideas of *significant figures* (the digits that are certain plus one more) with the notion of the percent uncertainty. We do not use just significant figures for the reasons developed in the next paragraphs.

We can cite two specific advantages of the significant figure designation of uncertainty.

1. It provides an easy introduction to the existence of uncertainty.

2. It provides an easy basis for making a crude estimate of the uncertainty propagated through multiplication and division.

These advantages must be weighed against four disadvantages.

1. *Significant figures furnish only a rough estimate of uncertainty.* For example, consider the three numbers 0.50 ± 0.01 , 0.90 ± 0.03 , and 1.10 ± 0.07 . In terms of significant figures, these would be written 0.50, 0.90, and 1.10, a notation that hides the fact that the uncertainties these numbers cast into a product would be, respectively, 2%, 3%, and 6%. Not only do the numbers expressed as significant figures fail to reveal that the uncertainty in 1.10 is three times that in 0.50; but they suggest that 1.10 is *less* uncertain.
2. *Significant figures omit reference to the accumulation of uncertainty as data are combined.* For example, the sum of 14 and 15 would be 29. All these numbers have two significant figures. However, if the addends are uncertain by ± 1 , the sum will be unknown to ± 2 . This absolute increase is not indicated at all by the form of the answer 29.
3. *The rules concerning significant figures used for multiplication are not applicable to other manipulations, notably addition and subtraction.* In addition and subtraction, the number of significant figures is *not* fixed by the number of figures known for the least precise datum. For example, consider the addition of two masses

$$m_1 = 1.10 \pm 0.01 \text{ g}$$

and

$$m_2 = 1000.0 \pm 0.1 \text{ g}$$

The sum,

$$m_1 + m_2 = 1001.1 \text{ g,}$$

has five significant figures, and the number of significant figures is determined by m_2 , though it has the larger number of significant figures. Contrast the subtraction of the mass of an empty flask, $m_1 = 160.02 \pm 0.01 \text{ g}$, from the

mass of the flask containing a sample, $m_2 = 160.83 \pm 0.01$ g. The difference, $m_2 - m_1 = 0.81 \pm 0.02$ g, has but two significant figures, not the same as either individual mass, m_1 or m_2 .

4. *Even in multiplication, the usual rules of significant figures can give erroneous indications of uncertainty.* Consider the two examples

$$(0.90 \pm 0.01)(1.15 \pm 0.01) = 1.04 \pm 0.02$$

and

$$(1.01 \pm 0.01)(1.03 \pm 0.01) = 1.04 \pm 0.02$$

In these two products, the uncertainties are the same, but the rules for significant figures, rigorously applied, would require that we round off the first answer to two significant figures and retain three figures in the second.

Despite these limitations we feel that good habits in the use of significant figures should be encouraged. As often as feasible, the student should be encouraged to express uncertainty explicitly (by adding $\pm$ to each measurement) and to estimate uncertainty in sums and differences, always using an appropriate number of significant figures. In referring to the use of significant figures as a basis for estimating the propagation of uncertainty, it must be emphasized that the method is applicable only in a general sense to multiplication and division, and is decidedly not applicable to addition, subtraction, or other mathematical manipulations.

Remind the student that if he gives too many significant figures, he is making an erroneous scientific statement—he is saying more than he knows to be true, possibly misleading himself and others. Thus, the matter of expressing uncertainty is much more than a formal set of rules; it is as important a part of the result of measurement as the result itself.

Some question may arise about the use of slide rules and logarithms as computational tools. Point out that inexpensive slide rules

give a precision of about 2–3 parts per 1000, whereas four-place logarithms provide a precision of about one part per 1000. The use of such tools limits the number of significant figures but not enough to be important in this course.

Some Omissions

Perhaps some omissions in the earliest chapters will seem unusual. They are omitted deliberately and with purpose.

1. Memorization, we feel, is tedious and should not be stressed as it misleads students into believing that this activity is science. There are too many chemical facts to remember, and they are doubling each decade. Students must get the basic concepts so they can apply them to the particular situation. On the matter of symbols and nomenclature, the student should learn the compounds he uses by seeing the names and symbols systematically associated in the text, on charts, and from your discussions.
2. History: we have placed emphasis on the contemporary aspects of chemistry. It is important to make the student keenly aware that he is preparing himself to deal with the scientific problems of today, not those of Dalton's time.
3. Eulogy: emphasis upon the "stroke of genius" tends to obscure the way in which science advances. It tends to exclude the student who feels no pretensions to genius. Emphasize instead that the great advances of chemistry made by the greatest of scientists can be understood by everyone, at least in retrospect. These great advances almost always are preceded by intensive, deliberate, and prolonged study.
4. Answers to some questions: some questions are raised and left unanswered in this chapter to make the student realize that there is a point to further study.

Answers to Exercises and Problems

Exercise 1-1

Figure 1-3 shows three cylinders with different cross-sectional areas. Mercury is poured into each of these cylinders until a depth of 10.0 cm is reached. Calculate the pressure in g/cm^2 at the bottom of each cylinder. The density of mercury is 13.5 g/cm^3 .

Answer

Pressure = mass/area

In each case the mass is found for a cylinder as

$$\frac{\pi r^2 h d}{\pi r^2} = hd \text{ and, numerically, is } 10.0 \text{ cm} \times 13.5$$

g/cm^3 or 135 g/cm^2

Exercise 1-2

- Add the values of the product PV in Table 1-2 and divide by 9 to obtain the average value.
- Now, on a separate piece of paper, make a fourth column for Table 1-2 showing the difference between each PV product and the average you have obtained in part a. Head this column with the word "Deviation." Make an entry, for each PV product minus the average value.
- Add the numbers in the column of deviations (disregarding algebraic signs) and divide by 9 to obtain an average deviation.
- Compare your calculations in parts a and c with the result in Table 1-2.

Answer

- a. sum = 201.2

Answer to Exercise 1-3

	Solution I	Solution II
estimate, A-B	35-40	37.5 ± 2.5 miles
estimate, B-C	45-55	50.0 ± 5.0
derived distance, A-C	80-95	87.5 ± 7.5 or 88 ± 8 miles
estimate, A-C	80-95	87.5 ± 7.5
estimate, C-D	30-35	32.5 ± 2.5
derived distance, A-D	110-130	120.0 ± 10.2 or 120 ± 10 miles

Exercise 1-4

Three students measure out different volumes of water, using a 25 ml graduated cylinder. After writing his value on the chalkboard, each student transfers his sample to a 100 ml beaker. The three samples are:

$$\begin{aligned} 22.5 \pm 0.5 \text{ ml} \\ 18.0 \pm 0.5 \text{ ml} \\ 24.0 \pm 0.5 \text{ ml} \end{aligned}$$

What is the total volume of water in the beaker and what is its uncertainty?

$$\frac{201.2}{9} = 22.355 \text{ or } 22.4$$

b. $P \times V$	deviation
22.4	0
22.2	-0.2
22.1	-0.3
23.0	0.6
22.4	0
22.2	-0.2
22.4	0
21.9	-0.5
22.6	0.2

- c. The sum of the deviations (ignoring minus signs) is 2.0

$$\frac{2.0}{9} = 0.222 \text{ or } 0.2$$

- d. Parts a and c give 22.4 ± 0.2 , as in Table 1-2.

Exercise 1-3

Three people give these estimates of the highway distance between towns A, B, C, and D.

A-B	35-40 miles
B-C	45-55 miles
C-D	30-35 miles

Give your estimate of the highway distance from A-C and from A-D.

(A to C, 80-95 miles)

Answer

Add the values and add the uncertainty. Total volume equals $64.5 \pm 1.5 \text{ ml}$.

Exercise 1-5

An engineer wished to determine the density of a new alloy of magnesium. He found that a sample weighed $33.35 \pm 0.01 \text{ g}$ and occupied $18.6 \pm 0.2 \text{ ml}$. Calculate the density and show the uncertainty.

Answer

$$\begin{aligned}\text{density} &= \text{mass/volume} = 33.4 \text{ g}/18.6 \text{ ml} \\ &= 1.80 \pm ? \text{ g/ml}\end{aligned}$$

The uncertainty in 18.6 ml is about 1% and that in 33.4 is negligible (about 0.03%). The uncertainty in the answer should be about 1% or 0.02 g/ml.

Problem 1

Name some conditions that should be controlled if you wish to determine how many miles different cars will travel per gallon of gasoline.

Answer

Conditions to control would include:

- mechanical adjustment of cars
- driving technique
- road conditions—surface, number of turns, hills
- weather—wind velocity and direction, temperature

Problem 2

Name some conditions that should be controlled if you want to determine the effectiveness of various detergents.

Answer

The factors to be controlled include:

- kind and amount of detergent used
- time of treatment
- temperature of water
- sample on which "dirt" is present
- hardness of water

Problem 3

Name some conditions that should be controlled if you want to determine the vitamin C content of various brands of frozen orange juice.

Answer

The factors to be controlled include:

- exposure of samples to air
- exposure of samples to sunlight
- all steps of the analytical procedure
- age of juice

Problem 4

Make a list of the regularities and the differences that you can observe among the various cars you know.

Answer

- All have 4 wheels, steering mechanism, engines, speed control.
- All can go forward or backward.
- All are made mainly of metal.
- All require fuel.
- They differ in color, age, state of repair, mass, comfort, number of doors, size, power of engine, shape.

Problem 5

Make a list of the regularities and differences that you can observe among the various soft drinks you know.

Answer

- All have flavoring.
- All contain a sweetener.
- All are liquids.
- They differ in flavor, color, size and shape of container, price, labels, names.

Problem 6

Make a list of the regularities and differences that you can observe among the different classrooms in your school.

Answer

- They all have doors and windows, place for teacher, chairs or other seats.
- They differ in size, shape, amount of chalkboard, special equipment available, arrangement of seats, teacher present.

Problem 7

Name some substances, not mentioned in this chapter, which are gases at room temperature.

Answer

Students might know the following gases which were not named in the chapter: butane, methane, nitrogen, acetylene, CO, CO₂, helium, neon, H₂S.

Problem 8

Hydrogen, helium, and carbon dioxide are gases at room temperature. What differences among the properties of these gases account for the following?

- (a) Hydrogen and helium are used in balloons but carbon dioxide is not.
- (b) Helium is less dangerous to use.

Answer

- (a) CO_2 is more dense than air.
- (b) Helium is not flammable.

Problem 9

A rock has a mass of 42.0 grams when it is weighed in air. When it is weighed in liquid carbon tetrachloride, the mass of the rock is 34.0 grams. Carbon tetrachloride has a density of 1.59 g/ml.

- (a) What is the volume of the rock?
- (b) What is the density of the rock?

Answer

- (a) The rock shows an apparent change in mass of 8.0 g. It displaced that mass of CCl_4 .

$$\frac{8.0 \text{ g}}{1.59 \text{ g/cm}^3} = 5.04 \text{ cm}^3 \text{ or } 5.0 \text{ cm}^3$$

- (b) The density of the rock is $\frac{42.0 \text{ g}}{5.0 \text{ cm}^3} = 8.4 \text{ g/cm}^3$

Problem 10

Calculate the density of an irregularly shaped object using these data. Water displacement was used to determine the volume of the object. Express your answer to the correct number of digits. (Use the value 1.00 g/ml for the density of water.)

Volume of water in a graduated cylinder, before the object was immersed.	20.0 ml
Volume of water in a graduated cylinder, after the object was immersed.	32.6 ml
Mass of the object in air.	34.0 g

Answer

The volume of the object is $32.6 - 20.0 = 12.6 \text{ ml}$.

$$\text{The density is } \frac{34.0 \text{ g}}{12.6 \text{ ml}} = 2.70 \text{ g/ml.}$$

Problem 11

Outline a method for determining the density of an object that floats on water.

Answer

The problem is to find the volume of the object. There are several ways depending on the object density and what is available.

If the object is a regular figure, determine its volume by measurement.

If the figure is irregular, immerse it in a liquid (less dense than water) in which it will sink. If no such liquid is available, push the object under with a thin wire or tie a mass of known volume onto it.

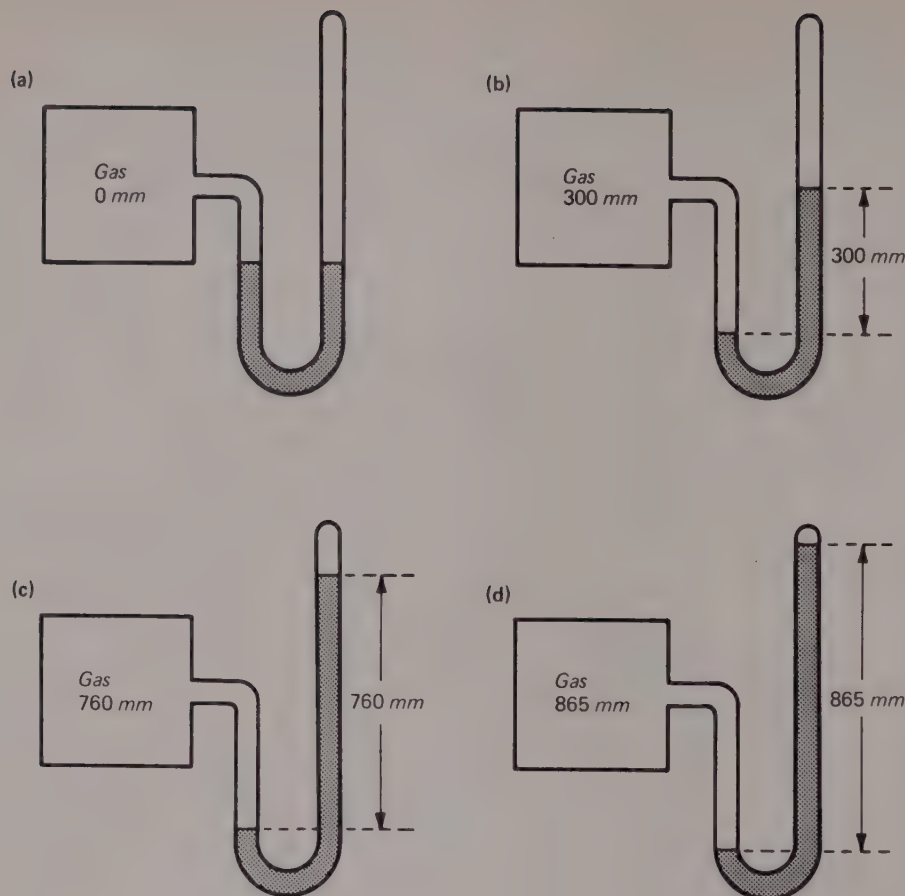
Problem 12

What do you think will happen to the mercury column in a barometer (Figure 1-4, page 6) if you do these things?

- (a) Tip the glass barometer tube away from its vertical position.
- (b) Carry the barometer up a high mountain.
- (c) Lower the barometer to the bottom of a swimming pool.

Answer

- (a) The top of the mercury will remain a fixed vertical distance (atmospheric pressure) above the bottom. In a tipped tube the length of slanting mercury will be greater than for the vertical column.
- (b) The mercury column will become shorter, showing the pressure is less.
- (c) The column will become longer because the pressure of the water is added to that of the atmosphere.



Answer to
Problem 13

Problem 13

Gas is slowly added to the empty chamber of a closed-end manometer (see Figure 1-5, page 7). Draw a picture of the manometer mercury levels, showing in millimeters the difference in heights of the two mercury levels:

- before any gas has been added to the empty gas chamber.
- when the gas pressure in the chamber is 300 mm.
- when the gas pressure in the chamber is 760 mm.
- when the gas pressure in the chamber is 865 mm.

Answer

See diagram above.

Problem 14

Repeat Problem 13, with an open-end manometer (see Figure 1-6, page 7). Use a value of 760 mm for atmospheric pressure.

Answer

See diagram on next page.

Problem 15

List three different units that could be used to express the speed of a spaceship.

Answer

Possible units are miles/hour, cm/sec, light years/year, kilometers/day, inches/century or any distance unit divided by any time unit.

Problem 16

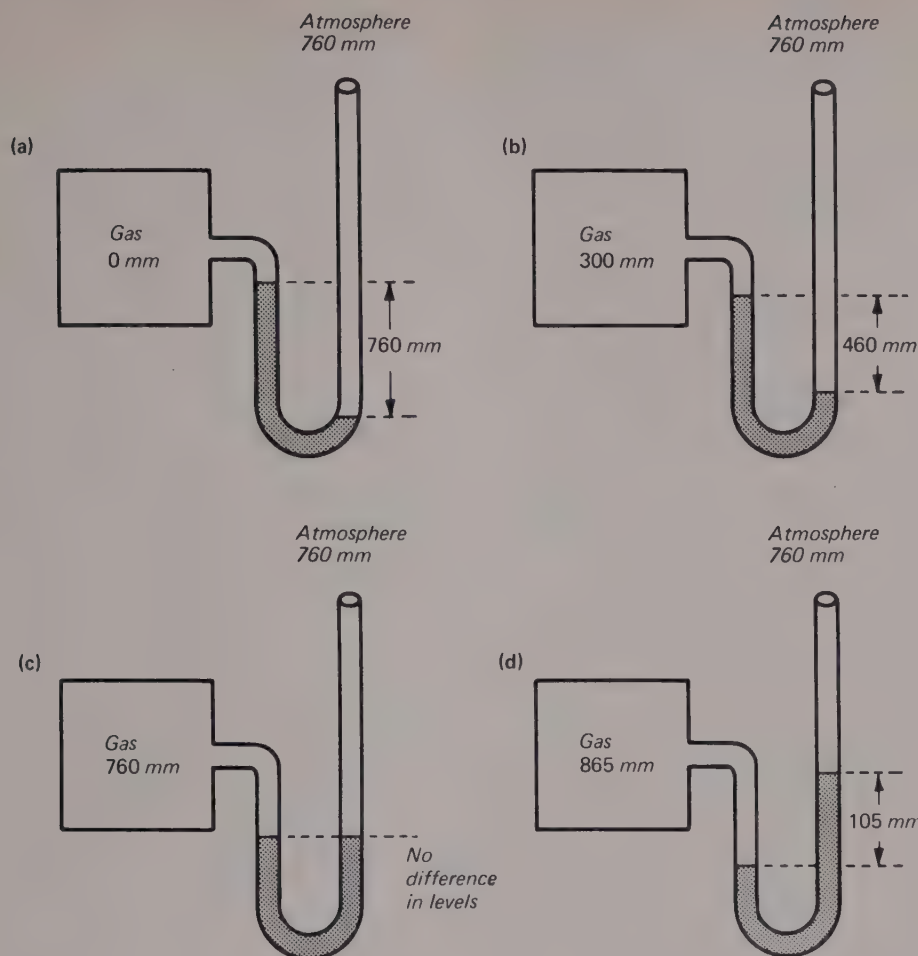
In studying the effect of pressure on the volume of a gas, why is it necessary to keep the temperature constant?

Answer

Because both pressure and volume will change if temperature does.

Problem 17

Suppose in the example of ball bearings shaken in the plastic box that very small ball bearings were used. Would



Answer to
Problem 14

it be so easy to detect a single collision? Would the pressure on the walls be much greater, much less, or approximately the same for the smaller ball bearings? Justify your answer.

Answer

Single collisions would not be easy to detect by sight or hearing. You can make the point that actual gas particles are invisible and collisions undetectable. If you assume the same amount of energy is fed into the balls by shaking, the pressure would remain the same.

Problem 18

Consider a box of ball bearings being shaken at a constant rate. What would happen to the number of collisions between ball bearings and walls if the box were made smaller?

Answer

A constant rate of shaking implies some average speed for the ball bearings. If the walls are closer together (smaller box), then the balls will strike the walls more often.

Problem 19

The balloons that are used for weather study are quite large. When they are released at the surface of the earth, they contain a relatively small volume of gas compared to the volume they acquire when aloft. Explain.

Answer

As a balloon rises, atmospheric pressure decreases. The gas volume in the balloon increases. (There are also temperature changes involved so that PV is not constant.) If the balloons were

filled at the start of the flight, the gas would be wasted as it spilled out in the upper atmosphere.

Problem 20

Give several examples of two variables that are related so that when one variable increases, the other decreases. Example, pressure and volume of a gas.

Answer

length and width of a constant area
the height of an elevator and the height of its counterweight
the heights of two ends of a seesaw
unit price and quantity bought (often not a linear relation)
the filled and empty spaces in a given volume
income taxes and take-home pay from a fixed salary

Problem 21

Express mathematically the relationship between the number of days you have lived and your age in years. Ignore the number of leap years that may have occurred during your lifetime. How could you modify your mathematical equation to take into account leap years?

Answer

total days = $(365) \times (\text{years})$

To allow partially for leap years

$$\text{total days} = (365)(\text{years}) + \frac{\text{years}}{4}$$

This formula is exact only if the number of years is divisible by 4.

To be exact a student must add one more day if:

1. he was born before Mar. 1 *or*
2. his birthday is Mar. 1 or later in the year *and*
 - a. years/4 has a remainder of 3 *or*

- b. years/4 has a remainder of 2 and he was born 1 or 2 years before a leap year *or*
- c. years/4 has a remainder of 1 and he was born 1 year before a leap year.

Problem 22

In 1960 a ten year Census of the United States was carried out. The population of a large city was stated to be 3,846,523. How do you react to that figure? How would you have reacted before you began to study this book?

Answer

The population figure is probably less well known than the seven significant figures given. There must have been deaths and new births during the tabulation. Some persons would be out of town, too sick to answer the door, or deliberately misrepresenting. In any event, the number will change in a few months. Perhaps $3,846,000 \pm 3000$ would be a more informative figure.

Before studying uncertainty, most students would accept the figure although everyone "rounds off" such numbers when reading or repeating them. This rounding was for convenience, not from an understanding of the uncertainty of measurement.

Problem 23

Which do you think would cost more, a cube of iron 1 inch on each edge or a cube of iron 1.000 inch on each edge? Why?

Answer

The cube of 1.000 inch edge would cost more. The time required to produce a block precise to 0.001 inch would add considerable cost above just sawing out one that was 1 inch on the edge.

Suggested Quiz Questions

These suggested questions are designed for a one-period open-book test. There are more than enough; hence some selection is required.

Observation is made solely by examining a burning candle.

1. Which of the following is an interpretation rather than an observation?
 - (1) The candle gives off light and heat as it burns.
 - (2) The wick is made of three strands of

string braided together.

- (3) The burning candle makes little or no sound.
- (4) The candle burns to produce carbon dioxide and water.
- (5) The top of the candle becomes wet with a colorless liquid, and the top becomes bowl-shaped.

Answer: (4).

2. Which of the above can be considered *quantitative* descriptions?

Answer: 2 and 3.

3. Which of the above can be considered *qualitative* descriptions?

Answer: 1 and 5.

In a group of students, each was directed to measure the temperature of a beaker of boiling water and that of a beaker of ice plus water, both to the nearest 0.2°C . Each was to use his own thermometer and record the readings at the board. The following data were obtained.

Student	Boiling Water Temp. $^{\circ}\text{C}$	Ice-Water Temp. $^{\circ}\text{C}$
1	98.8	0.4
2	99.0	0.0
3	98.6	0.2
4	98.4	-0.2
5	99.2	0.0
6	98.8	0.0
7	98.8	0.4

4. Using all of the data given, express the boiling water temperature using the form $\text{_____} \pm \text{_____}^{\circ}\text{C}$.

Answer: $98.8 \pm 0.2^{\circ}\text{C}$.

5. What is the uncertainty in the measurement for the ice-water temperature?
 $\pm \text{_____}^{\circ}\text{C}$.

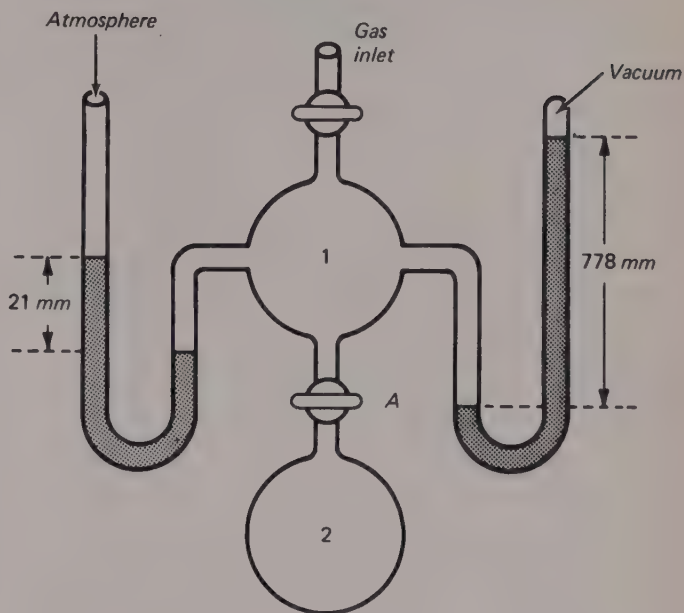
Answer: $\pm 0.2^{\circ}\text{C}$.

6. What is the uncertainty in the difference

between the boiling temperature and the melting temperature?

$\pm \text{_____}^{\circ}\text{C}$.

Answer: $\pm 0.4^{\circ}\text{C}$.



When the experiment starts, both valves are closed, bulb 1 has gas in it and bulb 2 (of equal size) is evacuated. Ignore the volumes in the manometer tubes.

7. The pressure of gas in bulb 1 is:

- (1) 21 mm of Hg
- (2) 778 mm of Hg
- (3) 799 mm of Hg
- (4) 757 mm of Hg
- (5) none of these

Answer: (2)

8. Atmospheric pressure is:

- (1) 21 mm of Hg
- (2) 778 mm of Hg
- (3) 799 mm of Hg
- (4) 757 mm of Hg
- (5) none of these

Answer: (4)

9. What will happen to the pressure when stopcock A is opened?

- (1) the left manometer will remain unchanged.
- (2) the right manometer will remain unchanged.
- (3) the left manometer will have a difference of 389 mm between Hg levels.
- (4) the right manometer will have a difference of 410 mm between Hg levels.
- (5) none of the above.

Answer

- (5) The pressure would drop to half of the starting value. The left manometer would register 11.5 mm Hg and the right one 389 mm Hg.

Listed below are the melting and boiling temperatures for some common substances.

Substance	M.T. °C	B.T. °C
Copper	1083	2582
Silver	961	2193
Iron	1535	2800
Moth balls	53	174
Sugar	112	—
Wax	53–55	282

10. What regularity seems to exist for the six melting temperatures?

Answer

The high melting temperatures belong to metallic substances.

11. Does this same regularity hold for the boiling temperatures listed?

Answer: Yes.

12. List two questions that are suggested to you as a result of "wondering why" about these data.

Answer

Student response, such as (1) Do all metals have high melting and high boiling temperatures? (2) Do all nonmetals have low melting and low boiling temperatures?

13. What is the density of an object if 83.6 grams of it occupies 14.3 ml of space?

Answer

$$D = \frac{M}{V} = \frac{83.6}{14.3} = 5.85 \text{ g/ml}$$

14. A metal spoon is found to have a mass of 27.63 g in air, and a mass of 24.48 g in water. What is the density of the metal? Silver has a density of 10.5 g/ml. Is the spoon pure silver?

Answer

27.63

24.48

3.15 g and hence ml of water displaced

$$\frac{27.63}{3.15} = 8.78 \text{ g/ml}$$

No, the spoon is not pure silver. (Possible alloying metals and their densities are Sn 7.28, Cu 8.92, and Zn 7.14 g/ml.)



Intent and Approach

In Chapter 2 the development of atomic theory does not follow a historical path but relies heavily on combining volume data instead of combining mass data. The logic of this approach is easier for the student and makes use of experimental data within his grasp at this time. The background Section (p. 30) details the argument and our reasons for preferring the method presented. That section should be read carefully.

The purpose of this chapter is twofold: to show growth of a theory and to introduce molecules via Avogadro's Hypothesis. Chapter 1 set the stage for the first goal through its particulate explanation of gases. Here the theme will be to show the scientific method in action. This is done by a few turns around the cycle of questions that asks what is implied; what experiment will give the needed data; what the results are; what change in theory is required; what this change implies; and so on.

The second goal is approached by showing that gases other than oxygen also give $PV = \text{constant}$. After finding that different masses are needed to give the same numerical constant, we wonder why. This leads us to look at some properties of gases, from which we can propose that molecules of different gases are different, and that their difference is due to variation in the atoms contained. From here it is a natural step to wondering about the mass of a molecule. By using combining volumes of gases together with Avogadro's Hypothesis we can provide an answer to this and also settle the diatomicity of O_2 , H_2 , and other gases. Symbols and formulas follow naturally.

The chosen arrangement permits each major concept to be preceded by experimental evidence—some obtained directly by the student and some shown in the film on gases or given in the Textbook.

Outline

The particle model of gases is used to correlate pressure-volume data for a gas (2-1). Other gases are found to give $PV = \text{constant}$, but different masses are needed to get the same numerical value of the constant. Wondering why this is true leads to two possible answers.

Experimental data on $NH_3 + HCl \rightarrow NH_4Cl$, plus a film on this and other reactions, leads to the regularity of combining volumes (2-2). Avogadro's Hypothesis gives the simplest explanation for the integral ratio of reacting volumes.

The relative mass (2-3) and number of atoms

per molecule (2-4) follow easily.

Elements and compounds are defined according to the kinds of atoms (2-5). Symbols are introduced.

Formulas and models are discussed (2-6).

The mole as a unit (2-7) is used to fix molar mass (2-8). These ideas provide the basis for some chemical calculations (2-9).

A review (2-10) summarizes.

New Concepts

1. Avogadro's Hypothesis.
2. Relative mass of molecules.
3. The mole.
4. Models of molecules.
5. Symbols and formulas.

Development

Demo. 2, MASS OF AIR,

fits here. See p. 18 in the Laboratory Guide.

Expt. 5, THE MASSES OF EQUAL VOLUMES OF GASES,

fits here. See p. 19 in the Laboratory Guide.

2-1 Implications and Growth of a Scientific Theory

This section uses the particle model of gases from Chapter 1 as a starting point for wondering about *PV* behavior. Make this and following

sections serve as examples of the steps in the scientific method given early in Chapter 1.

You should make an opportunity to tell the student clearly what is happening during this chapter. We are going through the typical growth of a model. It is at first devised to explain a particular property in a specified range of conditions. As other aspects of behavior or wider ranges of conditions are considered, the model is modified (sometimes replaced, but not in this instance). In practice, but not in this chapter, this process of revision is continued until all the behavior is adequately but usually not perfectly described or until the model is shown to be of so little value that it is discarded and a new one tried.

SCHEDULE AND RELATED MATERIAL

Suggested Time : 10 days

Text Section	Topic and Other Work	Exercises	Problems		
			Easy	Medium	Hard
2-1	Demo. 2. Mass of Air Expt. 5. Masses of Equal Volumes of Gases Growth of Scientific Theory Demo. 3. Kinetic Motion Demo. 4. Particle Model of Gases Demo. 5. Solubility of NH_3 or HCl Demo. 6. Reaction of NH_3 and HCl	1	1, 2		
2-2	Reacting Volumes Film Gases and How They Combine		3		
2-3	Relative Mass of Molecules	2	4		
2-4	No. Atoms in Molecules				
2-5	Elements and Compounds	3, 4	5-8		
2-6	Chemical Formulas Demo. 7. Construction of Molecular Models		9	10-12	
2-7	The Mole Demo. 8. The Size of a Mole of Water as a Liquid and as a Gas	6	13, 14, 16	15	17
2-8	Molar Mass	7-9	18		19-20
2-9	Calculations Based on the Mole Expt. 6. Iron-Copper Sulfate Reaction Expt. 7. Copper-Silver Nitrate Reaction Expt. 8. Conservation of Mass during Chemical Change	10, 11	29, 35-38	22-24, 27, 28, 30-34, 39-42	21, 25, 26
2-10	Review				

If you do not already have dissectible models of H_2 and O_2 for showing balancing of an equation, make some before Chapter 3. See p. 26 of the Laboratory Guide for instructions.

Demo. 3, KINETIC MOTION,

fits here. See p. 25 in the Laboratory Guide.

In this section we *assume* that the "push" of each collision is the same. You know, and the student may have observed from the demonstrations, that this is not so, and we will return to the point later. At this stage, however, it is a convenient assumption.

Note: This is not the time to start a discussion of gas laws (Chapter 4) or molecular structure (Chapters 10 and 16).

A second purpose of this section is to initiate the idea that the particles of different gases are different. The *PV* data are used to show that the most general regularity is found when different masses of gases are tested. *Remember:* the student is not yet aware of molar mass; these numbers are just those needed to make the same regularity fit each gas. From the different sample masses we are led to wonder about the masses of individual particles.

This section, together with the next few sections and Experiment 5, seeks to establish Avogadro's Hypothesis as a reasonable, simple explanation of a number of facts about gases. Emphasize the recurring method of approach. Our wondering why about $PV = k$ leads to some new explanations (A and B, p. 23). These in turn suggest new experiments which help make one explanation seem more probable than the other. The pattern of self-consistency defined by such "probabilities" found many times by different methods constitutes *scientific proof*. Chapter 8 of this Guide will go into detail about scientific proof.

Demos. 4-6 fit here.

PARTICLE MODEL OF GASES
SOLUBILITY OF NH_3 OR HCl
REACTION OF NH_3 AND HCl

See pp. 25-26 in Laboratory Guide.

2-2 Reacting Volumes of Gases

Film, GASES AND HOW THEY COMBINE,

fits here. See p. 29 for summary.

You will recognize the law of combining volumes, but let the film and text make the point. Notice also that the groundwork is being laid for reactions and equation balancing. Nevertheless, keep the focus of attention on the logic through which Avogadro's Hypothesis is implied by the integer volume ratios *without* reference to the actual reaction taking place. In fact, the argument becomes circular if it is predicated upon a knowledge of the chemical formulas, for these formulas are deduced from the hypothesis. Leave the development of chemical equations for Chapter 3, after symbols and formulas have been introduced.

2-3 Relative Masses of Molecules

Perhaps you have noted our consistent use of "mass" rather than "weight" when speaking of samples, particles, and molecules. The operation of determining mass is still called "weighing" because "to mass" is not a verb in English. To be consistent, some decision about the common phrase "molecular weight" was necessary. In Section 2-8 we will introduce "molar mass" for the mass of one mole. This new notation may require some change on your part. It has these advantages:

- Mass is the proper term for what we actually determine.
- Molar mass is parallel to molar volume, molar heat of reaction, and so on.
- It is more descriptive and shorter than "gram molecular weight," the older counterpart.
- The student has no prior bias toward either expression.

In any event, you should avoid saying "molar mass" in this section. Look at the advantages

of waiting until Section 2-8, after molecules have been further defined, the mole introduced, and the terms element and compound made clearer.

Point out that any gas *could* be taken for the standard (as oxygen was in the text). This matter of an arbitrary standard comes up repeatedly (ΔH in Chapter 10, and E° in Chapter 15).

2-4 The Number of Atoms in a Molecule

Students are often confused by the diatomic gases. "How do you know?" is a common question. The example shows the logic used on oxygen. It is probably worthwhile bringing up all the common diatomic gases (H_2 , O_2 , N_2 , F_2 , Cl_2 , Br_2 , I_2) if only to make the student familiar with them.

2-5 Substances: Elements and Compounds

It is probably best not to try for an extremely precise definition of the words *atom*, *element*, *molecule*, and *compound*. Your use of these terms and the stress on particles in Chapters 1 and 2 will suffice. Take copper, for instance. Ask for its properties (color, electrical conduction, heat conduction, density, malleability, etc.). The students will know these in a qualitative way. Show some less common elements from your stockroom, such as P, Na, Br_2 , Zn, and others. Emphasize that these are called elements because experiments show that they contain only one kind of atom.

Compounds are somewhat more difficult. Although almost everything we see is made of compounds rather than elements, many of the objects are mixtures, polymers, minerals, and natural products of complex (often unknown) structure. But these do not make good examples. The traditional ones are water, salt, and sugar. Others the student might know are alcohol (rubbing), baking soda ($NaHCO_3$), "hypo" ($Na_2S_2O_3 \cdot 5 H_2O$, sodium thiosulfate), epsom salts ($MgSO_4 \cdot 7 H_2O$, magnesium sulfate), and milk of magnesia [$Mg(OH)_2$, magnesium hydroxide]. Just show the compounds and name them; don't give formulas yet.

In general, we minimize the memorization of chemical formulas because they can be very misleading. $CuCl_2$ suggests that copper combines with two chlorine atoms. This occurs only in the gas phase, a condition seldom seen by beginners. In the solid, each copper is surrounded by six chlorine atoms, four at 2.3 Å and two at 2.85 Å. There are many other such examples. Also memorizing "valences" and formulas may lead the student to think compounds *obey* the combining rules implied. Exceptions are legion. Ni and S form NiS, but they also form Ni_3S_2 and Ni_6S_5 . Cobalt forms Co_9S_8 ! Chlorine and oxygen form Cl_2O , ClO_2 , and Cl_2O_7 , and maybe others. On the other hand, $NaHSO_3$ does not exist in stable form. Neither does NCl_5 , although PCl_5 is well known.

Stress the changes which compounds undergo to give different products that lead us to conclude that compounds contain more than one kind of atom. The Textbook treats water and sugar. You might demonstrate burning alcohol (to give water and CO_2) or put vinegar and baking soda together to give CO_2 . This will provide background material to be drawn upon in Chapter 3 when chemical reactions are introduced.

To a beginning student, chemical names and symbols are quite foreign. They should be treated as items of convenience. Encourage the students to learn the symbols, but don't force them to memorize a long list. Make their use seem so easy and important that the student feels he must learn them.

2-6 Chemical Formulas

The same treatment given elemental symbols should be used for formulas. Be sure to tie the written formula H_2O to the more pictorial drawings as well as to the stick and Styrofoam models. Prepare the students for different ways of representing formulas. Structural formulas come up specifically in this section and Figure 2-6 in the Textbook shows some.

You can assure the student that we will devote plenty of time toward understanding how the size, shape, and arrangement of atoms in

molecules are learned and on the benefits of such knowledge. *This is not the time to develop this knowledge.* Chapters 10 and 16 will give details, although there is much reference to models before these chapters. There will be considerable interest in these models. They will be used in Chapter 3 to illustrate the first balancing of an equation.

Demo. 7, CONSTRUCTION OF MOLECULAR MODELS

There is a discussion of model construction on p. 26 of the Laboratory Guide.

2-7 The Mole

See the Background Section (p. 32) for reasons why we stress the mole. We have used the basic definition of a mole as a mass of material and have commented on this use in the actual measurement of a mole. On the other hand, we have stressed the significance of the number of particles in a mole and have extended the concept to any particle. Thus, a mole is 6.0×10^{23} particles of any kind—for example, atoms, ions, electrons, molecules, or even people, dollars, or calories.

Demo. 8, THE SIZE OF A MOLE OF WATER AS A LIQUID AND AS A GAS

fits here. See p. 30 in the Laboratory Guide.

This use provides several advantages that teachers have found quite important:

- The idea of a mole goes over very easily.
- The mole method of working problems fits, in a helpfully obvious way, with balancing equations.
- Special units (equivalents, formula weights, combining weights) are not needed and should not be introduced.

The student should learn that the choice of the first molar mass is arbitrary. After that first

choice, the others are fixed experimentally, and Avogadro's number is also fixed. This point can be made in terms of alternate scales, as discussed in the Background Section, only convenience dictating which is used.

Questions may be asked about methods of determining Avogadro's number. The Background Section treats this point, indicating that chemists had no need to know N until the early nineteen hundreds when the details of the molecular model began to be explored. For the student, an answer based on Millikan's experiment (Chapter 6) and Faraday's Laws (Chapter 15) is most easily understood and closely tied with what he will study. The optimum explanation follows this line of logic: Later, you will study two sets of experiments. One determines the charge of a single electron; the other measures how much total charge is needed to cause one mole of silver atoms to plate out of solution as metal (a change which takes one electron per atom). By dividing as follows, we see that

$$\begin{aligned} \frac{\text{total charge/mole}}{\text{charge/electron}} &= \frac{\text{number of electrons}}{\text{mole}} \\ &= \frac{\text{number of atoms}}{\text{mole}} \\ &= \text{Avogadro's number} \end{aligned}$$

You may want to just list some of the other methods—X-ray diffraction, radioactive decay, Brownian motion—but discussion is not profitable, because the student lacks the proper background.

2-8 Molar Mass

A portion of the background material (p. 32) discusses ways to determine molar mass, but it is not intended that this be discussed in class. If a question does arise, stress the gas density method based on Avogadro's Hypothesis. The student will do (in Experiment 7) an experiment of the type that is used in determining many molar masses. Of course, in Experiment 5 he determined the molar mass of a gas, although that point could not be brought out then. Problem 26 makes the point.

Make sure the students know the relation between molar mass and Avogadro's number.

$$\text{molar mass} = \text{mass of } 6.0 \times 10^{23} \text{ particles}$$

2-9 Calculations Based on the Mole

This section should be used to give the student practice converting grams to moles and the reverse. This step is important in solving problems based on equations. Equations and problems using such conversions will come up throughout the course, so it is worth achieving a good understanding of this fundamental idea.

Empirical formulas provide some practice in the grams-to-moles conversion *and* stress the relation between moles and number of particles (atoms in this case). In addition, empirical

formulas can help you show that chemical formulas come from experiment and they appear later in Chapter 18 on organic substances.

Expt. 6, IRON-COPPER SULFATE REACTION,
fits here. See p. 31 in the Laboratory Guide.

Expt. 7, COPPER-SILVER NITRATE REACTION,
fits here. See p. 34 in the Laboratory Guide.

**Expt. 8, CONSERVATION OF MASS DURING
CHEMICAL CHANGE,**
fits here. See p. 37 in the Laboratory Guide.

Supplementary Material

Books

Bruce H. Mahan, *UNIVERSITY CHEMISTRY*, Addison-Wesley Publishing Co., Inc., Reading, Mass. (1965). The first two chapters deal with gases, atomic theory, and moles.

W. F. Kieffer, *THE MOLE CONCEPT IN CHEMISTRY*, Reinhold Publishing Corp., New York (1963). A book useful throughout the course.

Film

For ordering information see the *List of Film Sources* at the back of the Teacher's Guide.

GASES AND HOW THEY COMBINE

A CHEM Study film

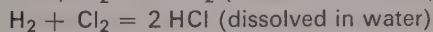
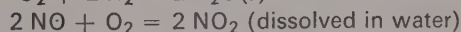
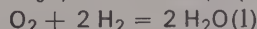
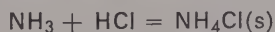
Running Time: 20 minutes

This film was produced in collaboration with Dr. G. C. Pimentel and fits quite closely with the Textbook, for which several figures are taken directly from the film.

The purpose of this film is to provide experimental evidence that can be used in the development of the atomic theory. The film presumes that the description

of a gas as a collection of particles has been established. The first portion of the film shows the great differences among gases: color, solubility in water, and combustibility are shown for NH_3 , Cl_2 , H_2 , HCl , NO , NO_2 , and O_2 . These observations furnish the basis for the conclusion that the particles (molecules) of different gases must be different.

The remainder of the experimental part of the film demonstrates the integer combining volume relations for the following reactions:



Having developed this evidence on combining volumes, the film narration is arranged in order that the film can be stopped as an "open-ended" presentation. Then you can develop Avogadro's Hypothesis through classroom discussion if you desire. On the other hand, the last section of the film draws the conclusion—Avogadro's Hypothesis—through additional narration. Show this part if you prefer, or else use it as a climax to the classroom discussion. Thus the film provides experimental support for Avogadro's Hypothesis.

Background Discussion

This section comprises discussions of the following topics:

Chemical Evidence for the Existence of Atoms
Interpretation of Combining Volume Data
What Is a Molecule?

Determination of Molar Mass

The Mole

Avogadro's Number (determination)

The Molar Mass Scales

The Naming of Chemical Elements

In Chapter 1, the particulate model of a gas is offered as an intuitively acceptable explanation of experimental facts known to the student. We are, quite frankly, building upon the student's readiness to accept the atomic theory on the basis of previous contact with the idea—through earlier science courses and through various communication media (even including the funny papers). Then, in Chapter 2, the particulate model is developed on the experimental base provided by the combining volumes of gases. The experiments are described in the Textbook and are actually shown in the film entitled GASES AND HOW THEY COMBINE.

This introduction to the atomic description of matter ignores historical chronology and differs from traditional treatments in which combining weights play a dominant role. A mature scientist believes in the usefulness of the atomic hypothesis because he himself has had innumerable successes in a wide variety of applications based on this hypothesis. From a scientist's point of view, it would be incorrect to single out one of these applications as *the* reason or even as the most important reason why he has such confidence in this theory. In a modern discussion of the experimental basis for belief in atoms, mass spectrometry, infrared spectroscopy, and a dozen other types of data are fully as important as are combining weights. To enumerate all or even several of these at the beginning of the course, without corroborating experiments, would hardly promote the experimental theme of this course.

For these reasons our task in Chapter 2 is not to present *the* evidence for atoms; *the* evidence is too diverse, too manifold, too esoteric. Rather, we must begin with a small part of the evidence and let the particulate model enlarge and become more positive as new facts are learned. Only after the student has a substantial background can we present anything resembling a full picture.

Chemical Evidence for the Existence of Atoms

The logic by which chemical evidence leads to the atomic hypothesis is direct.

1. *There are compounds and elements.* Operationally, an element is a substance that *cannot* be decomposed into two or more distinct substances, and a compound is a substance that *can* be decomposed into two or more distinct substances.
2. *Compounds* are found to have *definite composition* (in terms of the relative masses of the elements contained).
3. When two elements are found together in two different compounds, the relative masses are related by a simple whole-number ratio (*the law of simple multiple proportions*).
4. Gases react in simple proportions by volume, and the volume of any gaseous product bears a whole-number ratio to that of any gaseous reactant (*the law of combining volumes*).

The first evidence, that there are elements and compounds, is consistent with, but does not imply, the atomic hypothesis. This is shown by the fact that the differentiation between elements and compounds had been made for centuries before Dalton proposed the atomic hypothesis.

The second evidence raises a real question about the structure of matter. Why are compounds so particular about their composition? This question causes one to consider models of the structure of matter—models that would “explain” the definite composition of compounds.

Once again, however, the evidence is consistent (in an intuitively satisfying way) with the atomic theory, but does not suggest it by itself.

The third evidence *does* suggest the atomic hypothesis. Simple integer relationships suggest "units" or "portions." A given amount of oxygen can react with one portion of hydrogen, or with two portions, but not with 1.8732 portions. These simple integer relationships interweave all of chemistry. Thus the composition of NH_3 is simply related to the compositions of NO and H_2O_2 . For example,

0.0625 g hydrogen reacts with 1.000 g oxygen
(H_2O_2)

0.8750 g nitrogen reacts with 1.000 g oxygen
(NO)

3(0.0625) g hydrogen reacts with 0.8750 g
nitrogen (NH_3)

Such evidence naturally leads to a model involving "portions," "particles," or finally atoms.

The fourth evidence again involves, but in quite another way, simple integer relationships in that the volumes are related simply. Two volumes of hydrogen react with one volume of oxygen and produce two volumes of water vapor (all at the same temperature and pressure). Once again these integer relationships lead to models made up, somehow, of "units" or "portions" and point the way to the atomic hypothesis.

This last evidence is, by far, the simplest. It involves the integer relationships that lead to a particulate model without the need for aprior development of the concepts of elements and compounds. Furthermore, the arithmetic manipulations inherent in the combining mass argument are totally absent. These manipulations furnish a substantial obstacle to the student who does not feel confident in mathematics. Hence we have concluded that gas behavior offers the most readily assimilated basis for the atomic theory. Having thus proposed the theory, we are afforded an intuitively simple introduction to the ideas of balancing chemical equations, to mass relations, to a differentiation between elements and compounds, etc. Then, in later chapters, after the student has accumulated a

significant background of experience, we return to a review of the evidence for the atomic theory, beginning with already familiar chemical evidence. Even then, halfway through the course, the operation of a mass spectrometer is somewhat mysterious, but at least this complicated machine is mentioned only after an entire semester of laboratory work. Furthermore, this timely review of evidence for atoms can be presented in such a way that the student will see how a scientific theory gains general acceptance. Consistency among many kinds of data establishes confidence in a theory. Any single behavior must be interpreted within a web of premises. The credibility of the interpretation is attested by its reasonableness when viewed in the pattern of agreement with the other types of evidence.

Interpretation of Combining Volume Data

One of the most important goals of an introductory chemistry course is to encourage the student to think critically. To do so, we have maintained a tight and self-contained logic through the discussion of the combining volumes of gases.

For example, Exercise 2-3 considers the volume ratios in the reaction between hydrogen and chlorine to form hydrogen chloride. The conclusion of the exercise is that if chlorine molecules contain an even number of atoms, then hydrogen molecules must also contain an even number of atoms.

Initially, the treatment in Chapter 2 focuses on the types of conclusions that come directly from combining volume data. The integer ratios suggest the existence of molecules made up of atoms, and they help decide whether a given molecule contains an even or odd number of atoms. Later, when we distinguish between elements and compounds, we must face the question: How do we decide whether hydrogen is an element or a compound? The answer is that all attempts to show that the gas hydrogen is a compound must fail (that is, all attempts to decompose the compound into two distinct sub-

stances must fail). Thus it takes a large accumulation of experimental evidence to establish that hydrogen is an element (of which combining volume evidence is part). It takes only *one* experiment (and Avogadro's Hypothesis) to establish that each hydrogen molecule (no matter what atoms it contains) contains an even number of atoms *if* each chlorine molecule contains an even number (no matter what atoms the chlorine molecule contains).

What Is a Molecule?

A molecule is a collection of atoms held together with sufficient attractive force such that they can be treated as a unit under the conditions of study. This means the unit found in gaseous sodium chloride is a NaCl molecule, just as gaseous hydrogen chloride consists of HCl molecules. In principle, free radicals, gaseous ions such as H_2^+ , and ionic complexes in water, such as $\text{Ni}(\text{H}_2\text{O})_6^{2+}$, deserve to be called molecules as much as does benzene. We see that we have made an extremely broad definition of a molecule. This has been done deliberately for these two reasons:

1. There is only one cause for atoms to remain close together—the special attractive forces resulting from electrons being simultaneously attracted to two nuclei. (Chapter 10 develops this point.)
2. The species that are traditionally “stable” as molecules, ions, free radicals, and complexes are stable only because of the particular physical conditions available on our planet.

By using the broader definition we plan to keep the student's attention focused on the single cause of bonding and remind him that, at conditions different from those in our world, different molecules will be prevalent.

We *do not* propose to discard the terms ion, free radical, etc. used to specify certain kinds of molecules, but you should make a point of the similarities. Monatomic molecules should cause no trouble. They serve as the limiting case of a group of atoms.

Determination of Molar Mass

This subject may arise through questions—it is not intended that it be presented to the class at this early time. The molar mass of a gas is usually determined by some application of Avogadro's Hypothesis. The student will make such a determination in Experiment 5. You might indicate briefly the logical procedure in this fashion: We will assume that equal volumes of gases (at the same conditions) contain equal numbers of molecules. By weighing fixed volumes of two gases, we find their relative masses, and from these we can compute the molar mass of one gas *if* the other is known.

The molar mass of liquids and of soluble solids is usually found from colligative properties. The freezing and boiling temperatures of a solution differ from those found for the pure solvent. The lowering of the freezing or the rise in boiling temperature is proportional to the concentration of dissolved particles.

Compounds of very large molar mass (polymers and a number of biological materials such as proteins) require other methods. The most common are osmotic pressure, light scattering, viscosity, and sedimentation rates in ultracentrifuges.

The Mole

The mole is a concept of paramount importance. This importance comes from the great simplification that this concept gives to our understanding of the chemical equation and its meaning. As a result, all the operations based on an equation become quite easy. Balancing the equation is related directly to molecules (and the models used to illustrate them). Stoichiometric problems all have a *single* method of solution. Molar heat of reaction and other molar properties are easily understood.

In spite of the importance of the mole, or Avogadro's number of particles, it is strange that, for the chemistry met during the first semester, there is no need to know Avogadro's number. The chemist does not need to know *N* to solve

conventional problems (such as mass or concentration relations). He needs to know only that there *is* such a number.

There are many problems in modern chemistry for which the chemist does need to know N . Some examples are the determination of atomic dimensions, molecular structures, packing in crystals, and atomic energy levels. The methods outlined below for measuring N were first designed and performed by physicists.

Avogadro's Number

The French physicist Perrin undertook, in the early years of the twentieth century, a series of measurements on the Brownian motion of small particles of a natural gum, gamboge. The potential energy of a particle of mass m in a gravitational field with acceleration constant g is given by $E = mgh$; h is the height of the particle above some reference height measured in the direction of the field gradient. These can be combined to give

$$\frac{\Delta n}{n} = \frac{-mgN \Delta h}{RT} \quad (1)$$

in which Δn is the change in the number of particles per unit volume at two different heights separated by Δh . The other symbols have their earlier significance.

Perrin prepared uniform gum particles of mass m and observed their distribution in a suspending liquid as a function of height. Thus the only factor in equation (1) not susceptible to direct evaluation is N , and Perrin found this number to be 6.8×10^{23} molecules per mole. This number, which is 13% above the best currently accepted value, represented the first reliable value determined for N . It should be remarked parenthetically that Perrin was the first to use the term Avogadro's number (or constant).

An independent evaluation of N , suggested by E. Rutherford, was based on the amount of helium produced by the alpha decay of certain radioactive nuclides. A known quantity of radon gas (produced from radium) was enclosed in a thin-walled container, and the helium (produced

when radon undergoes radioactive disintegration) would diffuse through the walls of the container into a second volume previously pumped out to a high vacuum. By measuring the volume of helium gas produced during a known time interval, the fraction of a molar gas volume which this represented could be calculated. From the known decay constant of radon, it was possible to calculate the number of helium atoms that had been formed. From these data, Avogadro's number can be calculated from the relation

$$N = \frac{2.24 \times 10^4}{V_{\text{He}}} n(1 - e^{-(0.693t/t_{1/2})}) \quad (2)$$

in which V_{He} is the volume of helium collected (corrected to standard conditions) from the decay of n atoms of radon after a time t . The symbol $t_{1/2}$ in this relationship is the half-life of $^{222}_{86}\text{Rn}$ expressed in the same time units as t . The value of N calculated by Rutherford and his co-workers, particularly B. Boltwood and H. Geiger, was 6.16×10^{23} atoms per mole.

The first high-precision value for N was obtained on the basis of Millikan's determination of the magnitude of the electron charge, e . Millikan's experiments followed the reasoning laid down by Stokes and Perrin (and developed by Einstein) and were related to the measurements of settling rates of particles in a gravitational field. The earlier experiments, however, required an accurate knowledge of the viscosity of air and of the flow dynamics of gases, as well as a careful selection of particles of uniform size. Millikan avoided these problems by balancing the gravitational force downward with an electrostatic force upward. His observations could thus be confined to essentially stationary particles in an electric field.

The result of Millikan's experiments was a precise value of the electron charge, e , which could then be used to evaluate Avogadro's number from a relationship based on Faraday's law of electrolysis. Faraday had suggested that it was possible to define one mole of electrons as a definite quantity of electricity. This quantity is called one faraday, F , and represented in the

chemical literature by

$$F = Ne \quad (3)$$

The value of F can be readily determined from electrochemical experiments, and since such experiments involve only a sequence of weighings which can be carried out to a high precision, the numerical value of the faraday is well known. The value is 9.6519×10^4 coulombs/mole of electrons. With Millikan's value for e , it then became possible to calculate a reliable value for N from equation (3); that is

$$N = \frac{F}{e} = \frac{9.6519 \times 10^4 \text{ coulombs/mole}}{1.60203 \times 10^{-19} \text{ coulomb/electron}}$$

$$N = 6.023 \times 10^{23} \text{ electrons/mole} \quad (4)$$

We may complete the list of some representative methods which have been used to evaluate N by mentioning a calculation based on the X-ray determination of crystal parameters. Using the X-ray reflection technique it is possible to calculate the spacing, d , between adjacent layers of a regular crystalline solid. Let us illustrate this method by reference to sodium chloride, which crystallizes in a cubic lattice. A cube, or unit cell, of NaCl constructed with four chlorine atoms and four sodium atoms occupying the eight vertices will actually contain one-half of a sodium atom and one-half of a chlorine atom, since one-eighth of each atom is in the cell we are discussing. The cell has a side of 2.814×10^{-8} cm.

One mole of NaCl weighs 58.45 g and occupies $58.45/2.165 = 27.00 \text{ cm}^3$. The volume containing one Na and one Cl is $2(d)^3 = 4.457 \times 10^{-23} \text{ cm}^3$. Thus the number of NaCl units in one mole, N , is

$$\frac{27.00 \text{ cm}^3/\text{mole}}{4.457 \times 10^{-23} \text{ cm}^3/\text{NaCl unit}}$$

$$= 6.058 \times 10^{23} \text{ NaCl units/mole}$$

The difference between this value and the "best value" probably lies in the experimental diffi-

culty of getting crystals that have no void spaces or cracks.

The Molar Mass Scales

The choice of the first molar mass was an arbitrary one, and there is not unanimous agreement on the best choice. For a long time the chemist used a scale based on "naturally occurring" oxygen as 16.0000. A problem arose when it was later found that there are three isotopes (of mass number 16, 17, and 18) and that the isotopic composition of O_2 is not necessarily constant. The physicists then defined a scale based on $^{16}\text{O} = 16.0000$. For most chemical purposes the scales are equivalent, but they are not exactly equal (physical scale mass/chemical scale mass = 1.00027). Late in 1961 at least one international group agreed to use $^{12}\text{C} = \text{exactly } 12.0000$ as the standard. Such a standard has advantages because C ions are easy to measure in the mass spectrometer and carbon forms many high-mass molecule ions and hydrides which can act as standards up to high-mass numbers. Oxygen does not have these high-mass ions. Use of the ^{12}C scale implies a change of molar masses based on $\text{O} = 16.0000$ by a factor 0.9999550. Notice that discussion of these alternate scales will be more appropriate in Chapter 8, where isotopes are introduced. The chart inside the back cover is based on $^{12}\text{C} = 12.0000$.

The Naming of Chemical Elements

The nomenclature of elements is not a topic to which you should devote time. There are no rules for the names, and the classifications are of little help in studying chemical properties. An occasional, casual mention of the basis for a name can provide interest and a mental hook for remembering.

A number of substances which are today recognized as elements have been known to man for many centuries, some of them since before recorded history. Among these are the elements copper, silver, gold, iron, sulfur, lead, tin, mercury, and carbon. The names applied to these materials have been so firmly fixed in

the language that applying a particular "scientific" name has not been possible.

For the more recently isolated elements, the origin of their names falls roughly into three classes: *neoclassical*, *geographical*, and *honorary*. The neoclassical names, usually taken from Latin or Greek roots, are those applied in such a way that a chemical or physical property of the element is revealed thereby. The roots of helium and hydrogen are well known. Silicon is named for the Latin word *silix*, for flint.

The geographical group of names includes elements such as europium, holmium (after the Latinized form of Stockholm), lutetium (after a variant of the name of the patron saint of Paris), berkelium, californium, americium, francium, scandium (after Scandinavia), yttrium (after the town of Ytterby in Sweden), rhenium (after the Rhine River in Germany), and strontium (after the town of Strontian in Scotland).

The honorary names—largely applied to the most recent synthetic elements—include einsteinium, fermium, mendelevium, and lawrentium, as well as gadolinium and samarium.

A list of the origin of names can be found in *The Restless Atom*, by A. Romer, Doubleday, New York (1960). In *Discovery of the Elements*, a book published by J. Chemical Education, 1956, M. E. Weeks describes each element and the chemists associated with its isolation. The book contains some useful background information and may be of interest to some students.

Modern convention invests the discoverer or group of discoverers with the prerogative for suggesting a name for the new element. If the claim of discovery is recognized by the International Union of Pure and Applied Chemistry, the suggested name is usually adopted internationally. Official adoption does not, however, necessarily place the name of the element in general or undisputed usage. For example, the recently adopted official name for element 74 is wolfram. English and American chemists, among others, appear almost universally to prefer the name tungsten, and it is this appellation which appears most frequently in the technical literature of the English-speaking world.

Answers to Exercises and Problems

Exercise 2-1

If 32.00 grams of hydrogen chloride gas (at 0°C and one atmosphere) occupy 19.6 liters, then a larger mass of hydrogen chloride is needed to occupy the larger volume, 22.4 liters. Show that the mass needed is 36.5 grams.

Answer

Since 32.00 grams occupy 19.6 liters,

$$\frac{32.00 \text{ g}}{19.6 \text{ liters}} \times 22.4 \text{ liters} = 36.5 \text{ g}$$

Exercise 2-2

At 25°C and 1 atm pressure, one liter of neon gas weighs 0.83 gram. What is the mass of a neon molecule relative to the mass of an oxygen molecule (32.0)?

Answer

An oxygen molecule weighs more than neon by a factor of $\frac{1.31}{0.83}$.

$$\text{Mass of neon molecule} = 32.0 \times \frac{0.83}{1.31} = 20.2$$

Exercise 2-3

One volume of hydrogen gas reacts with one volume of chlorine gas to form two volumes of hydrogen chloride gas. What can you say about the number of atoms in one molecule of hydrogen? of chlorine? of hydrogen chloride?

Answer

Hydrogen and chlorine must have an even

number of atoms in their molecules. If they had an odd number, the atoms could not be divided so as to form two identical hydrogen chloride molecules.

We cannot say anything about the number of atoms per molecule of hydrogen chloride except that there must be at least one of each kind.

Exercise 2-4

What differences between water, oxygen, and hydrogen can you point out from your own experience? For example, you might consider

- (a) boiling and melting temperatures,
- (b) role in combustion,
- (c) role in supporting life.

Answer

- (a) Water boils at 100°C and freezes at 0°C. The student will probably not know these properties for oxygen and hydrogen, but he should know that these gases boil at much lower temperatures than 0°C.
- (b) Oxygen is needed for combustion—water hinders it, although it is usually a product of combustion.
- (c) Oxygen and water are needed for life. Hydrogen gas is not.

Exercise 2-5

Carbon dioxide has the formula CO_2 . Remembering that the prefix "di" means two, and "tri" means three, write the molecular formula for each of the following substances: carbon disulfide, sulfur dioxide, sulfur trioxide. (If you don't know the symbol for an element, use the table inside the back cover of the book.)

Answer

carbon disulfide: CS_2
 sulfur dioxide: SO_2
 sulfur trioxide: SO_3

Exercise 2-6

Since a mole of oxygen weighs 32.0 grams, how much would one million oxygen molecules weigh? Why was a mole not defined as one million molecules?

Answer

$$\left(\frac{32.0 \text{ g/mole oxygen}}{6.0 \times 10^{23} \text{ molecules/mole}} \right) (10^6 \text{ molecules}) = 5.3 \times 10^{-17} \text{ g}$$

This mass is much too small to be weighed out. A practical sized mole must weigh enough so that the error in weighing is negligible.

Exercise 2-7

Show that the mass of a mole of NO_2 is 46.0 grams and that the mass of a mole of SO_2 is 64.1 grams.

Answer

A mole of NO_2 molecules contains one mole of nitrogen atoms and two moles of oxygen atoms. It weighs $14.0 + 2(16.00) = 46.0 \text{ g}$.

A mole of SO_2 molecules contains one mole of sulfur atoms and 2 moles of oxygen atoms. It weighs $32.1 + 2(16.00) = 64.1 \text{ g}$.

Exercise 2-8

What is the molar mass of each of the following substances: sulfur (formula, S_8), ammonia (formula, NH_3), and nitrogen (a diatomic molecule)?

Answer

One mole of S_8 weighs

$$8 \times (32.1) = 256.8 = 257 \text{ g}$$

One mole of NH_3 weighs

$$14.01 + 3(1.008) = 14.01 + 3.024 = 17.03 \text{ g}$$

One mole of N_2 weighs

$$2(14.01) = 28.02 \text{ g}$$

Exercise 2-9

Calculate the mass of 6.0×10^{23} molecules of carbon monoxide, CO .

Answer

There are 6.0×10^{23} molecules in one mole of CO . One mole of CO weighs

$$12.0 + 16.0 = 28.0 \text{ g}$$

Exercise 2-10

How many moles of iron atoms are present in 1.67 grams of iron? How many iron atoms are present in 1.67 grams of iron?

Answer

$$\frac{1.67 \text{ g iron}}{55.8 \text{ g/mole iron}} = 0.030 \text{ mole iron}$$

$$\begin{aligned} & (0.030 \text{ mole}) \left(6.0 \times 10^{23} \frac{\text{atoms}}{\text{mole}} \right) \\ & = 1.8 \times 10^{22} \text{ atoms in 1.67 g iron} \end{aligned}$$

Exercise 2-11

A compound contains 6.0 grams of carbon for each 2.0 grams of hydrogen. Convince yourself that the empirical formula is CH_4 for this compound.

Answer

$$\frac{6.0 \text{ g carbon}}{12 \text{ g/mole C atoms}} = 0.50 \text{ mole carbon}$$

$$\frac{2.0 \text{ g hydrogen}}{1 \text{ g/mole H atoms}} = 2.0 \text{ moles hydrogen}$$

$$\frac{2.0 \text{ moles hydrogen}}{0.50 \text{ mole carbon}} = 4.0$$

There are four times as many moles of hydrogen atoms as moles of carbon atoms. The empirical formula is CH_4 .

Problem 1

How could you make money buying argon gas at \$1.00 per liter and selling it for \$0.50 per liter?

Answer

Lower the pressure to less than $\frac{1}{2}$ an atmosphere. The volume will more than double.

Problem 2

Four differences between helium gas and nitrogen gas are listed below.

- Dry air contains 80% nitrogen but only 0.0005% helium (by volume).
- Helium is much less dense than nitrogen.
- Helium has much lower solubility in water than nitrogen has.
- Helium is much more expensive than nitrogen.

Which difference could account for the fact that a deep-sea diver is much less likely to suffer from the bends if he breathes a mixture of 80% helium and 20% oxygen than if he breathes air? (The bends is a painful, sometimes fatal, condition caused by the formation of gas bubbles in the veins and consequent interruption of blood flow. The bubbles form from gas dissolved in the blood at high pressure.)

Answer

- Helium-oxygen mixtures are used for diving at extreme depths because the low solubility of helium in the blood (which is mostly water) reduces the likelihood of the bends.

Problem 3

The most important step in the process for conversion of atmospheric nitrogen into important commercial compounds used for fertilizers or explosives involves the combination of one volume of nitrogen gas with three volumes of hydrogen gas to form two volumes of ammonia. From these data alone and Avogadro's Hypothesis, how many molecules of hydrogen combine with one molecule of nitrogen? How many molecules of ammonia are produced for each molecule of nitrogen?

Answer to Problem 3

one volume of nitrogen	combines with	three volumes of hydrogen	to give	two volumes of ammonia.
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Therefore, by Avogadro's Hypothesis,

one molecule of nitrogen	combines with	three molecules of hydrogen	to give	two molecules of ammonia.
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Problem 4

Gaseous uranium hexafluoride is important in the preparation of uranium as a source of "atomic energy." A flask filled with this gas is weighed under certain conditions of temperature and pressure. The mass of the gas is found to be 3.52 grams. The same flask is filled with oxygen gas and is weighed under the same conditions. The mass of the oxygen is found to be 0.32 gram.

- What is the ratio of the mass of one uranium hexafluoride molecule to the mass of an oxygen molecule?
- State any guiding principles needed in answering the question.

Answer

The equal volumes contain equal numbers of molecules if Avogadro's Hypothesis is assumed. Therefore,

$$\begin{aligned} & \frac{\text{mass uranium hexafluoride molecule}}{\text{mass oxygen molecule}} \\ &= \frac{\text{mass uranium hexafluoride gas}}{\text{mass oxygen gas sample}} \\ &= \frac{3.52}{0.32} = 11 \end{aligned}$$

Problem 5

A white substance, on heating, forms a colorless gas and a purple solid. Is the substance an element or a compound? Why?

Answer

Since at least two substances were formed, as shown by the two different products, the original substance must have been a compound.

Problem 6

What do the following symbols represent? K, Ca, Co, CO, Pb, Hf, HF.

Answer

K represents one atom or one mole of atoms of the element potassium.

Ca represents one atom or one mole of atoms of the element calcium.

Co represents one atom or one mole of atoms of the element cobalt.

CO represents one molecule or one mole of molecules of a compound containing one atom of carbon and one atom of oxygen in each molecule.

Pb represents one atom or one mole of atoms of the element lead.

Hf represents one atom or one mole of atoms of the element hafnium.

HF represents one molecule or one mole of molecules containing one atom each of hydrogen and fluorine in each molecule.

Problem 7

Here are the names of some common chemicals and their formulas. What elements does each compound contain?

(a) hydrogen peroxide	H ₂ O ₂
(b) jeweler's rouge	Fe ₂ O ₃
(c) light bulb filament	W
(d) tetraethyl lead	Pb(C ₂ H ₅) ₄
(e) baking soda	NaHCO ₃
(f) octane	C ₈ H ₁₈
(g) household gas	CH ₄

Answer

- hydrogen, oxygen;
- iron, oxygen;
- tungsten;
- lead, carbon, hydrogen;
- sodium, carbon, oxygen, hydrogen;
- carbon, hydrogen;
- carbon, hydrogen.

Problem 8

For each of the following substances, give the name of each kind of atom present and the total number of atoms represented in the formula.

Name	Formula
(a) graphite (pencil lead)	C
(b) diamond	C
(c) sodium chloride (table salt)	NaCl
(d) sodium hydroxide (lye)	NaOH
(e) calcium hydroxide	Ca(OH) ₂
(f) potassium nitrate	KNO ₃
(g) magnesium nitrate	Mg(NO ₃) ₂
(h) sodium sulfate	Na ₂ SO ₄
(i) calcium sulfate	CaSO ₄

Answer

Note that the point of the problem is to establish familiarity with the symbols.

Elements	Total number of atoms shown
(a) carbon	1
(b) carbon	1
(c) sodium, chlorine	2
(d) sodium, oxygen, hydrogen	3
(e) calcium, oxygen, hydrogen	5
(f) potassium, nitrogen, oxygen	5
(g) magnesium, nitrogen, oxygen	9
(h) sodium, sulfur, oxygen	7
(i) calcium, sulfur, oxygen	6

Problem 9

All of the following substances are called "acids." What element do they have in common?

(a) nitric acid	HNO ₃
(b) hydrochloric acid	HCl
(c) acetic acid	HC ₂ H ₃ O ₂
(d) sulfuric acid	H ₂ SO ₄
(e) phosphoric acid	H ₃ PO ₄

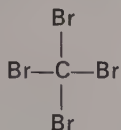
Answer

All of the substances contain hydrogen.

Problem 10

What does the molecular formula CBr₄ mean?

What additional information is provided by the structural formula?

**Answer**

Four atoms of bromine are combined with one atom of carbon to form one molecule of carbon tetrabromide.

Each of the bromine atoms is individually attached to the carbon atom. Note that this type of structural formula does not suggest exact spatial arrangements.

Problem 11

Write formulas for these compounds.

silicon dioxide
sulfur dichloride
nitrogen trifluoride
aluminum trifluoride
dinitrogen difluoride

Answer

SiO₂, SCl₂, NF₃, AlF₃, N₂F₂.

Problem 12

Write formulas for these compounds.

hydrogen chloride
hydrogen bromide
hydrogen iodide
boron trichloride
carbon tetrachloride
nitrogen trichloride
oxygen dichloride

Answer

HCl, HBr, HI, BCl₃, CCl₄, NCl₃, OCl₂.

Problem 13

How many particles are there in a mole?

Answer

6.0×10^{23} particles.

Problem 14

How many moles of oxygen atoms are in one mole of nitric acid molecules? Of sulfuric acid molecules?

Answer

The molecular formula of nitric acid is HNO₃. Hence one mole of nitric acid molecules contains three moles of oxygen atoms. A mole of sulfuric acid, with molecular formula H₂SO₄, contains four moles of oxygen atoms.

Problem 15

If we had one mole of pennies to divide among all the people in the world, how many dollars would each of the three billion inhabitants receive?

Answer

Population = 3 billion persons = 3×10^9 persons

$$\frac{6.0 \times 10^{23} \text{ pennies}}{3 \times 10^9 \text{ persons}} = 2.0 \times 10^{14} \text{ pennies/person}$$

This is 200,000 billion pennies or 2000 billion dollars for each person.

Problem 16

How many moles of people are there on earth?

Answer

$$\frac{3 \times 10^9 \text{ people}}{6.0 \times 10^{23} \frac{\text{people}}{\text{mole}}} = 5 \times 10^{-15} \text{ mole of people}$$

Problem 17

If there were a mole of people evenly distributed over the surface of the earth, including both land and sea, how many square inches would be allotted to each person?

Answer

The diameter of the earth is about 8000 miles.

$$\text{Area} = 4\pi r^2 = (4)(3.14)(4000 \text{ miles})^2$$

$$\text{or in inches} = (4)(3.14)(4000 \times 5280 \times 12)^2$$

Rounding π to 3 and simplifying gives

$$\begin{aligned} \text{area} &= (12)(4 \times 10^3 \times 5.3 \times 10^3 \times 12)^2 \\ &= 12(254.5 \times 10^6)^2 \\ &= 12(2.5 \times 10^8)^2 \\ &= 75 \times 10^{16} \text{ sq inches} \end{aligned}$$

$$\frac{7.5 \times 10^{17} \text{ sq in.}}{6 \times 10^{23} \text{ people}} = 1.3 \times 10^{-6} \text{ sq in./person}$$

or *one millionth* of a square inch per person.

Problem 18

What is the mass in grams of one silver atom?

Answer

Since 6.0×10^{23} silver atoms weigh 108 grams, one atom will weigh

$$\frac{108 \text{ g/mole}}{6.0 \times 10^{23} \text{ atoms/mole}} = 1.8 \times 10^{-22} \text{ g/atom}$$

Problem 19

A liter of chlorine gas is 2.22 times as heavy as a liter of oxygen gas when both are measured at room temperature and pressure. Calculate the molar mass of chlorine. How does this value compare with the molar mass of atomic chlorine, found in the table of molar masses? What is the formula of a molecule of chlorine?

Answer

(a) By Avogadro's Hypothesis, equal volumes (at the same T and P) contain equal numbers of molecules. Hence the ratio of the masses

of equal volumes is the same as the ratio of the molar masses.

$$\frac{\text{molar mass chlorine}}{\text{molar mass oxygen}} = \frac{\text{mass 1 liter chlorine}}{\text{mass 1 liter oxygen}} = 2.22$$

$$\text{molar mass chlorine} = (2.22)(32.00) = 71.1 \text{ g/mole}$$

(b) The molar mass of chlorine is 35.5 g/mole of atoms.

$$\frac{71.1}{35.5} = 2.00 \frac{\text{moles of atoms}}{\text{mole of molecules}}$$

or 2.00 atoms/molecule. The formula of a chlorine molecule is Cl_2 .

Problem 20

Suppose chemists had chosen a billion billion (10^{18}) as the number of particles in one mole. What would the molar mass for molecular oxygen be?

Answer

The mass of one oxygen molecule is

$$\frac{32.0}{6.0 \times 10^{23}} \text{ g}$$

Thus the mass of 10^{18} molecules would be

$$\frac{32.0}{6.0 \times 10^{23}} \times 10^{18} = 5.3 \times 10^{-5} \text{ g}$$

Problem 21

If $1\frac{1}{2}$ moles of hydrogen gas (H_2) react in a given experiment, how many grams of hydrogen does this represent?

Answer

$$\text{moles} \times \frac{\text{g}}{\text{mole}} = \text{g}$$

$$1.5 \times 2.0 = 3.0 \text{ g H}_2$$

Problem 22

Calculate the molar mass for each of these substances: SiF_4 , HF , Cl_2 , Xe , NO_2 .

Answer

SiF_4	$28.1 + 4(19.0)$	$= 104.1 \text{ g/mole}$
HF	$1.0 + 19.0$	$= 20.0 \text{ g/mole}$
Cl_2	$2(35.5)$	$= 71.0 \text{ g/mole}$
Xe	131.3	$= 131.3 \text{ g/mole}$
NO_2	$14.0 + 2(16.0)$	$= 46.0 \text{ g/mole}$

Problem 23

Write the formulas for these compounds and give the mass of one mole of each.

carbon disulfide
sulfur hexafluoride
nitrogen trichloride
osmium tetroxide

Answer

CS_2 76.2 g;
 SF_6 146.1 g;
 NCl_3 120.5 g;
 OsO_4 254.2 g.

Problem 24

Consider the following data:

Element	Molar mass of atoms
<i>A</i>	12.01
<i>B</i>	35.5

A and *B* combine to form a new substance, *X*. If four moles of *B* combine with one mole of *A* to give one mole of *X*, then the mass of one mole of *X* is:

- (a) 47.5 grams
- (b) 74.0 grams
- (c) 83.0 grams
- (d) 154.0 grams
- (e) 166.0 grams

Answer

(d) $12.01 + 4(35.5) = 154.0$ g.

Problem 25

A flask of gaseous CCl_4 was weighed at a measured temperature and pressure. The flask was flushed and filled with oxygen at the same temperature and pressure. The mass of the CCl_4 vapor will be about:

- (a) the same as that of oxygen.
- (b) one-fifth as heavy as the oxygen.
- (c) five times as heavy as the oxygen.
- (d) twice as heavy as the oxygen.
- (e) one-half as heavy as the oxygen.

Answer

The molar mass of CCl_4 is 154.0 g/mole. The CCl_4 vapor will weigh $154.0/32.00 = 4.814$, or about five times the mass of oxygen. Choice (c) is the correct answer.

Problem 26

In Experiment 5 you calculated the ratio of the mass of carbon dioxide to the mass of the same volume of oxygen.

Molecular oxygen has been assigned a molar mass of 32.0 grams. From the molar mass of oxygen and your measured ratio, calculate the molar mass of carbon dioxide. Estimate the uncertainty in your result. Compare the value you obtain with the molar mass of CO_2 calculated on page 34.

Answer

Let us assume that a particular mass ratio obtained in Experiment 5 for equal volumes of carbon dioxide and oxygen was

$$\frac{\text{g carbon dioxide gas}}{\text{g oxygen gas}} = 1.37$$

A molar mass contains 6.0×10^{23} molecules, which by Avogadro's Hypothesis occupies a fixed volume (for a given *T* and *P*). Consequently a molar mass ratio will be a ratio of masses of equal volumes of gas:

$$\frac{\text{molar mass carbon dioxide}}{\text{molar mass oxygen}} = 1.37$$

$$\begin{aligned} \text{molar mass carbon dioxide gas} &= 1.37 \times 32.0 \\ &= 43.8 \text{ g/mole} \end{aligned}$$

The weighing uncertainty should be near 5 or 6%. Since this number is used in a product with 32.0, a defined number, the relative uncertainty should be the same in the student's answer. Acceptable values would be 44 ± 3 g, or $43.8 \text{ g} \pm 6\%$.

Problem 27

A glass bulb weighs 108.11 grams after all of the gas has been removed from it. When filled with oxygen gas at atmospheric pressure and room temperature, the bulb weighs 109.56 grams. When filled, at the same pressure and temperature, with a gas sample obtained from the mouth of a volcano, the bulb weighs 111.01 grams. Which of the following molecular formulas for the volcano gas could account for the data?

CO_2 SO_3
 OCS S_8
 Si_2H_6 A gas mixture, half CO_2 and half Kr.
 SO_2
 NF_3

Answer

The two weighed gas samples contain the same number of molecules (by Avogadro's Hypothesis). Hence, the masses are in the ratio of the molar masses.

$$\begin{aligned}\text{Mass oxygen sample} &= 109.56 - 108.11 \\ &= 1.45 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{Mass volcano gas sample} &= 111.01 - 108.11 \\ &= 2.90 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{Molar mass volcano gas} &= \frac{2.90}{1.45} \times 32.00 \\ &= 64.0 \text{ g/mole}\end{aligned}$$

(Notice that there is no need for an air buoyancy correction because the same buoyancy effect is obtained in each weighing, and they cancel out in the subtraction.) The molar masses of the various possibilities are as follows:

CO ₂	44.0	SO ₃	80.1
OCS	60.1	S ₈	256.0
Si ₂ H ₆	62.2	CO ₂ + Kr	$\frac{44.0 + 83.8}{2} = 63.9$
SO ₂	64.1		
NF ₃	71.0		

Thus either SO₂ or the CO₂-Kr mixture could account for the data.

Although it was not requested, notice that the experimental uncertainty in the weighings introduces about 2% uncertainty in the molar mass determination. Thus the 62.2 g/mole molar mass of Si₂H₆ is just outside the range defined by the uncertainty.

Problem 28

A chemist weighs out 10.0 grams of water, 10.0 grams of ammonia, and 10.0 grams of hydrogen chloride. How many moles of each substance does he have?

Answer

The molecular formulas are H₂O, NH₃, and HCl.

Substance	Molar Mass
H ₂ O	$16.00 + 2(1.008) = 18.02 \text{ g/mole}$
NH ₃	$14.01 + 3(1.008) = 17.03 \text{ g/mole}$
HCl	$35.5 + 1.008 = 36.5 \text{ g/mole}$

$$\frac{\text{mass}}{\text{molar mass}} = \text{moles}$$

$$\text{H}_2\text{O} \quad \frac{10.0}{18.02} = 0.555 \text{ mole}$$

$$\text{NH}_3 \quad \frac{10.0}{17.03} = 0.587 \text{ mole}$$

$$\text{HCl} \quad \frac{10.0}{36.5} = 0.274 \text{ mole}$$

Problem 29

How many moles of atoms are there in 9.0 grams of aluminum? In 0.83 gram of iron?

Answer

(a) 27 g of aluminum contain one mole of aluminum atoms

$$9.0 \text{ g} = \frac{9.0 \text{ g}}{27 \text{ g/mole}} = \frac{1}{3} \text{ mole}$$

(b) 56 g of iron contain one mole of iron atoms

$$0.83 \text{ g} = \frac{0.83 \text{ g}}{56 \text{ g/mole}} = 1.5 \times 10^{-2} \text{ mole}$$

Problem 30

How many moles are there in 49 grams of H₂SO₄?

Answer

The molar mass of H₂SO₄ is

$$32.1 + 4(16.00) + 2(1.008) = 98.1 \text{ g/mole}$$

$$\frac{\text{mass}}{\text{molar mass}} = \frac{\text{g}}{\text{g/mole}} = \text{moles}$$

$$\frac{49}{98.1} = 0.50 \text{ mole}$$

Problem 31

The most delicate balance can detect a change of about 10⁻⁸ gram. How many atoms of gold would there be in a sample of that mass?

Answer

$$1 \text{ mole gold} = 6.0 \times 10^{23} \text{ gold atoms} = 197 \text{ g}$$

$$\text{g} \times \frac{\text{mole}}{\text{g}} \times \frac{\text{atoms}}{\text{mole}} = \text{atoms}$$

$$10^{-8} \times \frac{1}{197} \times 6.0 \times 10^{23} \\ = 3 \times 10^{13} \text{ gold atoms in } 10^{-8} \text{ g}$$

Problem 32

A stone about the size of a softball weighs roughly one kilogram. How many moles of such stones would be needed to account for the entire mass of the earth, about 6×10^{27} grams?

Answer

$$6 \times 10^{27} \text{ g} = 6 \times 10^{24} \text{ kg} \\ \text{Moles of stones} = \frac{6 \times 10^{24} \text{ kg}}{6 \times 10^{23} \text{ kg/mole}} \\ = 10 \text{ moles of stones}$$

Problem 33

How many atoms are in a copper penny (mass 2 grams)?

Answer

$$\left(\frac{2 \text{ g Cu/penny}}{63.5 \text{ g/mole Cu}} \right) 6.0 \times 10^{23} \text{ atoms/mole} \\ = 0.19 \times 10^{23} \text{ or } 2 \times 10^{22} \frac{\text{atoms}}{\text{penny}}$$

Problem 34

How many grams of table sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) are needed to supply one molecule for each of the 3×10^9 people on earth?

Answer

$$\text{Molar mass of } \text{C}_{12}\text{H}_{22}\text{O}_{11} \\ = (12 \times 12) + (22 \times 1) + (11 \times 16) \\ = 144 + 22 + 176 \\ = 342 \text{ g} \\ \left(\frac{3 \times 10^9 \text{ persons} \times 1 \frac{\text{molecule}}{\text{person}}}{6 \times 10^{23} \text{ molecules/mole}} \right) \left(342 \frac{\text{g}}{\text{mole}} \right) \\ = 171 \times 10^{-14} \text{ or } 2 \times 10^{-12} \text{ g required}$$

Problem 35

Acetylene gas is used in welding. Acetylene contains 30 grams of carbon for each 2.5 grams of hydrogen. What is the empirical formula for acetylene?

Answer

$$\frac{30 \text{ g C}}{12 \text{ g/mole C}} = 2.5 \text{ moles C} \\ \frac{2.5 \text{ g H}}{1 \text{ g/mole H}} = 2.5 \text{ moles H} \\ \text{empirical formula CH}$$

Problem 36

There are two common oxides of sulfur. One contains 32 grams of sulfur for each 32 grams of oxygen. The other oxide contains 32 grams of sulfur for each 48 grams of oxygen. What are the empirical formulas of these oxides?

Answer

$$\frac{32 \text{ g S}}{32 \text{ g/mole S}} = 1.0 \text{ mole S} \\ \frac{32 \text{ g O}}{16 \text{ g/mole O}} = 2.0 \text{ moles O} \\ \text{empirical formula SO}_2 \\ \frac{48 \text{ g O}}{16 \text{ g/mole O}} = 3.0 \text{ moles O} \\ \text{empirical formula SO}_3$$

Problem 37

A variety of phosphorus called red phosphorus is used in match heads. It burns to produce an oxide, 0.142 gram of the oxide containing 0.062 gram of phosphorus. What is the empirical formula of this oxide?

Answer

$$\text{mass O} = 0.142 - 0.062 = 0.080 \text{ g} \\ \frac{0.062 \text{ g P}}{31 \text{ g/mole P}} = 0.002 \text{ mole P} \\ \frac{0.080 \text{ g O}}{16 \text{ g/mole O}} = 0.005 \text{ mole O} \\ \text{empirical formula P}_2\text{O}_5$$

Problem 38

There are two known compounds containing only tungsten and carbon. One is the very hard alloy, tungsten carbide, used for the edges of cutting tools. Analysis of the two compounds gives for one, 1.82 grams of tungsten per 0.12 gram of carbon, and for the other compound, 3.70 grams of tungsten per 0.12 gram of carbon. What are the empirical formulas for these compounds?

Answer

$$\frac{1.82 \text{ g W}}{184 \text{ g/mole W}} = 0.010 \text{ mole W}$$

$$\frac{0.12 \text{ g C}}{12 \text{ g/mole C}} = 0.010 \text{ mole C}$$

empirical formula WC

$$\frac{3.70 \text{ g W}}{184 \text{ g/mole W}} = 0.020 \text{ mole W}$$

empirical formula W₂C

Problem 39

Equal volumes of oxygen and gas A are compared at the same temperature and pressure.

The mass of oxygen = 0.64 gram

The mass of gas A = 3.42 grams

- (a) Calculate the molar mass for gas A.
 (b) Given the empirical formula for gas A, CF₂Cl, what is the molecular formula for this gaseous substance?

Answer

$$\left(\frac{3.42 \text{ g A}}{0.64 \text{ g O}_2} \right) \left(\frac{32 \text{ g O}_2}{\text{mole O}_2} \right) = 171 \text{ g/mole A}$$

molar mass of empirical formula
 $= 12 + 2(19) + 35.5 = 85.5$

thus the empirical unit is $\frac{85.5}{171} = 0.5$ the molecular unit

molecular formula = 2(CF₂Cl) = C₂F₄Cl₂

Problem 40

Gas A, a compound containing nitrogen and oxygen, was compared to gas B in an experiment. Equal volumes of gas A and gas B are compared at the same temperature and pressure.

Mass of gas A	0.56 gram
Mass of gas B	0.30 gram
Molar mass of gas B	16.0 grams

- (a) Which of these oxides of nitrogen is gas A?
 N₂O, NO, NO₂, N₂O₃, N₂O₅.
 (b) Gas B is a compound containing only carbon and hydrogen. What is the molecular formula for gas B?

Answer

(a) $\left(\frac{0.56}{0.30} \right) (16.0) = 29.8$ or 30 g/mole A

molar mass of

N ₂ O	44
NO	30 = gas A
NO ₂	46
N ₂ O ₃	76
N ₂ O ₅	108

- (b) molar mass B = 16 g
 one mole of carbon atoms = 12 g
 thus hydrogen accounts for 4 g

$$\frac{4 \text{ g}}{1 \text{ g/mole H}} = 4 \text{ moles H}$$

molecular formula CH₄

Problem 41

In Problem 40(a), the formulas for five different nitrogen oxides are listed. For each of these, calculate the oxygen to nitrogen mass ratio, $\frac{\text{g oxygen}}{\text{g nitrogen}}$. Show that these ratios are themselves in the ratio of small whole numbers. What does this tell you about the mass of oxygen for a fixed mass of nitrogen in these compounds? This regularity is sometimes called the Law of Multiple Proportions.

Answer

gas	g oxygen/g nitrogen	value relative to 0.572
N ₂ O	0.572	1
NO	1.142	2
NO ₂	2.290	4
N ₂ O ₃	1.718	3
N ₂ O ₅	2.868	5

The last column of numbers tells us that compounds of oxygen and nitrogen are observed to have 0.5726 g O/g N or a simple whole number times this value.

Problem 42

In addition to water, hydrogen and oxygen form a compound called hydrogen peroxide, H_2O_2 . Calculate the ratio of grams of oxygen to grams of hydrogen for one mole of these two compounds. Compare the relative masses of oxygen in these two compounds. Does this comparison illustrate the Law of Multiple Proportions?

Answer

a mole of H_2O_2 has 32 g O and 2 g H

	g O/g H	value relative to B
H_2O	8	1
H_2O_2	16	2

Yes, these compounds illustrate the Law of Multiple Proportions.

Suggested Quiz Problems

These suggested questions are designed for a one-period open-book test. There are more than enough; hence some selection is required.

Consider the following model for a gas. The gas is a spongy material—like foam rubber. When it is compressed, the force exerted increases; but when it is released, it expands again.

1. Which of the following experimental evidence is NOT consistent with this proposed model?

- (1) A gas fills the container.
- (2) Increasing the pressure causes the volume to decrease.
- (3) Increasing the amount of gas increases the pressure.
- (4) A gas has mass.
- (5) When the gas is compressed and cooled it changes into a liquid.

Answer: (5).

2. Describe the changes that occur when a gas is treated in the following ways:

- (1) A sample of gas is compressed at a constant temperature.
- (2) Gas is added to a steel container at a constant temperature.

Answer

- (1) The volume decreases.
- (2) The pressure increases.

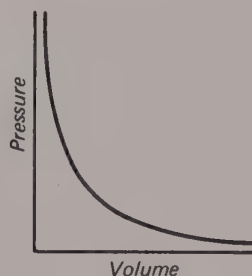
3. Draw a curve representing the following relations for a gas:

(1) Pressure vs volume (temperature and amount constant).

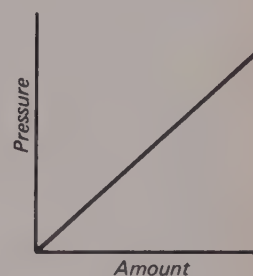
(2) Pressure vs amount (volume and temperature constant).

Answer

(1)



(2)



4. How many moles of each kind of atom are in a mole of each of the following molecules?

- (1) H_2SO_4
- (2) NO_2
- (3) CO_2
- (4) CH_3COOH

Answer

- (1) 2 moles H atoms; 1 mole S atoms; 4 moles O atoms.
- (2) 1 mole N atoms; 2 moles O atoms.
- (3) 1 mole C atoms; 2 moles O atoms.
- (4) 2 moles C atoms; 4 moles H atoms; 2 moles O atoms.

5. Assume that we have equal volumes of two different gases, *A* and *B*, at the same temperature and pressure. The sample of gas *A* weighs 1.60 g, and the sample of gas *B* weighs 3.55 g.

- (1) What is the mass of one molecule of *B* as compared to one molecule of *A*?
- (2) Assume that gas *A* is oxygen. What is the molar mass of gas *B*?

Answer

$$(1) \frac{3.55 \text{ g of } B}{1.60 \text{ g of } A} = 2.22$$

One molecule of *B* is 2.22 times as heavy as one molecule of *A*.

- (2) $(32 \text{ g/mole}) \times 2.22 = 71.0 \text{ g/mole}$, the molar mass of *B*.

6. How many grams are contained in one mole of each of the following?

- (1) Sodium chloride, NaCl (table salt).
- (2) Water, H₂O.
- (3) Silver, Ag.
- (4) Potassium nitrate, KNO₃.
- (5) Magnesium sulfate, MgSO₄.

Answer

- (1) 58.5 g/mole
- (2) 18.0
- (3) 107.9
- (4) 101.1
- (5) 120.4

7. How many atoms are contained in a mole of each of the following?

- (1) Sulfuric acid, H₂SO₄.
- (2) Calcium hydroxide, Ca(OH)₂.
- (3) Nitrogen dioxide, NO₂.
- (4) Acetic acid, CH₃COOH.
- (5) Sucrose, C₁₂H₂₂O₁₁.

Answer

- (1) $7 \times 6.0 \times 10^{23}$ atoms/mole.
- (2) $5 \times 6.0 \times 10^{23}$ atoms/mole.
- (3) $3 \times 6.0 \times 10^{23}$ atoms/mole.
- (4) $8 \times 6.0 \times 10^{23}$ atoms/mole.
- (5) $45 \times 6.0 \times 10^{23}$ atoms/mole.

8. How many molecules are there in 16.0 grams of methane (CH₄)?

$$\text{Answer: } 6.0 \times 10^{23}.$$

9. The following tests were made:

- (1) A white solid was heated gently, producing a gas which was partially condensed to a colorless liquid and a second white solid.
- (2) A dark-purple solid was heated gently in a vacuum, producing a purple vapor. The solid disappeared, leaving no residue.
- (3) A single white solid is formed from two colorless gases. On heating the solid the two gases are re-formed.

In which tests are compounds formed?

Answer

In (1) and (3). In (2) there is no evidence for more than one substance taking part or forming. In fact the vaporization of iodine is described.

10. How many moles of water molecules are there in 180 grams of water?

Answer

$$1 \text{ mole H}_2\text{O} = 18 \text{ g};$$

therefore

$$180 \text{ g H}_2\text{O} = 10 \text{ moles.}$$

11. What is the mass of a single molecule of water?

Answer

$$\frac{18}{6.0 \times 10^{23}} = 3.0 \times 10^{-23} \text{ g}$$

12. In an experiment similar to Experiment 7, a strip of zinc metal, Zn, was placed in an aqueous solution of lead nitrate, Pb(NO₃)₂. A spontaneous change took place in which 10.4 grams of lead were formed and the zinc strip lost 3.3 grams.

If a mole of Pb weighs 207.2 grams and a mole of Zn weighs 65.4 grams, how many moles of each metal were involved in the change? What is the relationship between moles involved?

Answer

$$10.4 \text{ g} \times \frac{1 \text{ mole Pb}}{207.2 \text{ g}} = 0.050 \text{ mole Pb}$$

$$3.3 \text{ g} \times \frac{1 \text{ mole Zn}}{65.4 \text{ g}} = 0.050 \text{ mole Zn}$$

For each mole of lead that changes, one of zinc also changes.

3. Knowing cadmium forms two oxides, CdO and Cd₂O, a chemist analyzed a 2.41 g sample and found 0.16 g oxygen and 2.25 g cadmium. Which oxide did he have?

Answer

$$\frac{0.16 \text{ g oxygen}}{16 \text{ g/mole oxygen}} = 0.010 \text{ mole}$$

$$\frac{2.25 \text{ g Cd}}{112.4 \text{ g/mole Cd}} = 0.020 \text{ mole}$$

$$\frac{\text{moles Cd}}{\text{moles O}} = \frac{0.020}{0.010} = 2$$

Formula of the compound is Cd₂O.

4. Three volumes of hydrogen are required to combine completely with one volume of nitrogen to form two volumes of ammonia. Suppose we combine one mole of hydrogen with one mole of nitrogen.

- (1) Are both gases used up in the process?
- (2) If not, which gas remains? How much?
- (3) How many moles of ammonia are formed?

Answer

- (1) Using Avogadro's Hypothesis, we can see from the volume data that three molecules of hydrogen combine with one molecule of nitrogen to form two molecules of ammonia. Since we start with a mole of each gas, both gases are not used up in this process.
- (2) $\frac{2}{3}$ mole of nitrogen remains, since one mole of hydrogen requires only $\frac{1}{3}$ mole of nitrogen.
- (3) $\frac{2}{3}$ mole of ammonia is formed, since the volume of ammonia formed is twice the volume of nitrogen ($2 \times \frac{1}{3}$).

15. Why is a correct formula more valuable to a chemist than the name of the substance?

Answer

The formula shows the elements that are present and the relative amounts of each element. Some formulas show the arrangement of the particles in the substance. This information is very useful in studying the reactions that substances may undergo. Some names tell nothing of the composition, whereas others reveal some or all of it.

16. One mole of carbon tetrabromide has all the following properties but one. Identify the exception.

- (a) It contains 5 moles of atoms
- (b) Together all the atoms in it weigh 332 g
- (c) It contains 4 bromine atoms
- (d) It contains 6×10^{23} carbon atoms
- (e) The carbon atoms in it weigh 12 grams

Answer

Part (c) is incorrect. Each molecule has four bromine atoms but each *mole* contains $4 \times 6 \times 10^{23}$ bromine atoms.

Principles of Chemical Reactions



Intent and Approach

In this chapter you should develop the student's understanding of elements, compounds, molecules, equations, and moles. This is the point at which to introduce the mole method of working problems, but not the place for extensive drill. The mole method should just grow from the balanced equation. Balancing equations is also not to be heavily emphasized as a technique. Rather, it should follow as a natural thing from the

conservation of atoms—as readily visualized with the molecular models you use to illustrate reactions. The balancing should seem an important but simple step in writing a correct set of symbols to express experimental knowledge. Use models to show how balancing is a simple but important step. Emphasizing the meaning of an equation is a good way to summarize these ideas.

Outline

Chemical reactions are introduced via the decomposition and formation of water (3-1, 3-2).

Conservation of mass (3-3) leads to equa-

tions (3-4, 3-5).

Section 3-6 deals with calculations based on equations.

New Concepts

1. Conservation of mass.
2. Use of the mole in solving problems.
3. How changes in matter are shown by equations and the meaning of the equation.

SCHEDULE AND RELATED MATERIAL

Suggested Time : 7 days

Text Section	Topic and Other Work	Exercises	Problems		
			Easy	Medium	Hard
3-1	Note 1 Formation of Water Demo. 9. Models for Showing Equation Balancing	1-3			
3-2	Decomposition of Water		6		
3-3	Conservation of Mass		1-3, 5, 10	4, 7, 9, 11, 20	
3-4	Equations		8		
3-5	Writing Equations	4, 5	12-14,	15-18,	19,
3-6	Calculations from Equations	6-8	21, 22, 30	23, 24, 28, 29	25-27, 31
3-7	Review				

Note 1. Expt. 9, The Formula of a Hydrate, can be done anytime during this chapter. See p. 45 in the Laboratory Guide.

Development

3-1 Formation of Water from Hydrogen and Oxygen

Demo. 9, MODELS FOR SHOWING EQUATION BALANCING,

fits here. See p. 43 in the Laboratory Guide.

3-2 Decomposition of Water

These sections are the student's first real look at some chemical reactions. Therefore, make an effort to show them fully. Demonstrate the reactions, and write equations, illustrating as many as you can by using models which can be reassembled to show conservation of atoms. Some student may want to know why he cannot have a lone oxygen atom left over. The best answer to this question comes from experiment: lone oxygen atoms haven't been found (in any substantial amount); therefore oxygen atoms must be very reactive.

Do not fail to bring the heat of reaction into your discussion. Chapter 8 will develop the subject, but this is the place to make the student aware that he must account for it. He will already know, in a rough way, several kinds of reactions which give out heat—burning things; dissolving some things; adding water to some solids (lime, plaster of Paris); metabolic use of food—and some that require energy—boiling water (or other liquids); dissolving some solids (hypo); melting solids.

Students also know that atomic explosions and nuclear fusion involve conversion of mass to energy. Such knowledge may help you tie this section to the next.

3-3 Conservation of Mass

Chemists do not ordinarily deal with nuclear reactions. Therefore the statement—"There is no detectable change in the quantity of matter during a chemical change."—is a statement of

the practical situation. Chemists know there are some exceptions. Changes in total mass have been measured. Treat these as important cases but outside the experimental ability of your class.

You can use the conservation of atoms *plus* the lack of conservation of molecules to illustrate again that molecules are clusters of atoms. Some common analogies are:

A constant number of marbles can be arranged in various numbers of piles.

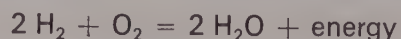
A constant number of bricks can make different numbers of objects.

A constant number of bread slices can make several numbers of sandwiches (open-face, regular, or double-decker).

3-4 Equations for Chemical Reactions

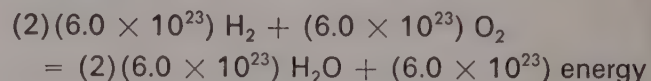
Here is the place to make extensive use of the molecular models. The entire idea of balancing an equation should be expressed in terms of physical objects. This makes the concept quite easy for the student. Go through several simple equations using the models.

Equation writing should flow as a natural result of conservation laws and the models you have used. The point to stress here is the meaning of the equation. This can be developed on at least two levels. In a general way the equation represents what happened. (*Note:* We can write an equation only after the products are known—by experiment or by coordinating rules based on actual tests.) Thus the first step toward an equation is an expression of chemical fact: hydrogen reacts with oxygen to give water and energy, or, in symbols, $\text{H}_2 + \text{O}_2$ gives $\text{H}_2\text{O} + \text{energy}$. We “balance” the expression to agree with experience, which says that we cannot destroy or create matter, and the equals sign, or arrow, is put in to express the conservation of atoms:

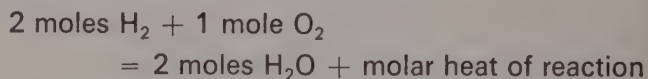


At this stage the statement becomes an equation *and* takes on a molecular meaning. From the models used we know this equation expresses the reaction of 2 *molecules* of hydrogen with one *molecule* of oxygen to give two *molecules* of

water (plus some energy). Now we fall back on our knowledge of arithmetic. We can double an equation, and it will still be true. Triple it, multiply it by 10, by 1000, or by 6.0×10^{23} , and it will still be true. Thus we can write



But this is a long way of writing



Hence the equation also shows the relative number of moles of chemicals involved. *Make sure the student sees and understands this dual meaning of an equation.* Avoid laying too much stress on the energy term, but use it to set up the idea for later.

3-5 Writing Equations for Reactions

This section provides practice with the ideas of the previous two. Concentrate on the meaning rather than any mechanics of balancing. Stress the molar implication of the equation to help the student in the next section.

3-6 Calculations Based on Chemical Equations

The mole relation expressed by an equation is the key to working any problem based on that equation. The mole method involves these steps:

1. Write and balance the equation.
2. Use the equation to find how many moles of desired substance are related to one mole of the given one.
3. Use step 2 and the moles of given substance to find the moles of desired substance formed.

At the beginning and end of many problems another step is sometimes needed.

convert from $\left\{ \begin{array}{l} \text{given units to moles, or} \\ \text{moles to desired units.} \end{array} \right.$

This conversion is not part of the mole method

but is a unit conversion problem added on. It is, however, of practical importance because we measure chemicals in grams or cubic centimeters or other units but almost never in moles.

At this stage emphasize the mole method and its advantage—a *single way to approach all problems based on equations*. It is best to keep conversions simple—use only grams $\rightarrow$ moles and moles $\rightarrow$ grams—until later. The student should be assigned problems based on equations in *every* chapter and test. This will provide the constant drill needed for mastery. Initially, place emphasis on problems of two types:

1. How many moles of *A* will react with *y* grams of *B* by the reaction . . . ?

2. How many grams of *A* will be produced from *y* moles of *B* by the reaction . . . ?

The mole method is the fundamental way to work problems—fundamental in that it is tied directly to the experimental meaning of a chemical equation. This method, with its three steps, is easy for the student because it is uniform for all problems *and* because the logical connections to the equation and its balancing, and to the molecular models, are made clear.

The so-called proportion method is actually the mole method with the supporting framework unstressed. As a result, it is not nearly so clear to a beginner. Do not use it.

Supplementary Material

Book

J. A. Campbell, WHY DO REACTIONS OCCUR?,

Prentice-Hall, Inc., Englewood Cliffs, New Jersey (1965).

Background Discussion

The Introduction of the Atomic Theory

The primary goal of this course is to convey an understanding of the nature of science. The next most important goal—and the minimum goal of any introductory chemistry course—is to convey to the student the meaning of balanced chemical equations, which embody the central idea of chemistry. A balanced equation describes a possible chemical reaction; a chemist must understand all of the implications, the properties, and the controlling conditions that are involved.

Consider the equation



It tells an experienced chemist that there is a possible reaction and that, if it occurs, then:

(a) Exactly two molecules of water are produced for every two molecules of hydrogen consumed and for every one molecule of oxygen

consumed.

- (b) Exactly two moles of water are produced for every two moles of hydrogen consumed and for every one mole of oxygen consumed.
- (c) There are 36.03 grams of water produced for every 4.04 grams of hydrogen consumed and for every 32.00 grams of oxygen consumed.
- (d) The system will change. Initially it is characterized by a set of properties that identify two substances, hydrogen and oxygen; finally it will be characterized by an entirely different set of properties—those that identify a third substance, water.

We have chosen to inform the student that the reaction given implies (a), (b), (c), and (d) by placing in his hands molecular models. A student might be given a single model of O_2 and the instructions "Fill out a check-out slip

for the number of models of H_2 needed to rearrange the O_2 model into as many H_2O models as possible." Ninety-five percent of the students will immediately count how many hydrogen atoms are required and ask for two molecular models of H_2 . The other 5% will ask for one model of H_2 , go back to their desks, and quickly notice that they have an atom of oxygen left over. They will return for another H_2 model. There, without any discussion, each student has balanced his first chemical equation. Every time, thereafter, that he must balance an equation, his thoughts will be guided by this first experience. Conceptually, he will never experience difficulty in balancing a chemical equation.

Assume that there are 25 students in the class and that we passed out 25 models of O_2 . If we ask how many total H_2O models were formed by the class, even the least perceptive student will have no difficulty answering "50" when he is looking at the two H_2O models he himself formed using one model of O_2 . How many from a dozen models of O_2 ? How many from one million models? How many from 6.0×10^{23} models?

Thus, the application of an equation to a larger number of molecules (e.g., a mole) is as easy, conceptually, as balancing the equation. But these models represent atoms, each of which has a characteristic mass. What mass of water will be formed from the one molecule of O_2 ? The student will readily see that it is the mass of two atoms of oxygen and four atoms of hydrogen. What mass of water is formed from one *mole* of O_2 ? It will be the mass of two *moles* of oxygen atoms and four *moles* of hydrogen atoms. Where can these masses be found? They are in a table inside the back cover. They are called molar

masses. Very quickly the student can comprehend the mass relations implied by the chemical equation.

The conceptual ease with which the student can grasp all the implications of the chemical equation, given the molecular models, explains why we begin this course with an authoritarian presentation of the atomic theory. Its success in the classroom justifies the approach: the conclusion (a) is easy to grasp; it readily leads to the mole concept (b); and the mass relationships (c) are all implied.

Historically, of course, the logic was the opposite of that presented here. The changes in properties (d) led to the identification of substances. A multitude of mass relationships (c) were needed before enough evidence was available for the inductive step which Dalton performed in deciding there must be atoms, implying (b) and (a). This is a difficult line of reasoning, even in retrospect. It presents the student with an intellectual test that many will fail. In return for hewing to the line of logic, we sacrifice facility in using and understanding the chemical equation.

What about the experimental approach? Yes, we have here deserted our wish to avoid an authoritarian presentation of the principles of chemistry. It is a deliberate act—done for what seems to be a crucially important gain. Tell the student this; encourage him to keep asking what evidence there is for the assumed atomic theory. He will hear the atomic theory referred to many times, and will use it to interpret many experimental observations. By the time he finishes later chapters and a detailed discussion of the experimental basis for the atomic theory, he will know the evidence.

Answers to Exercises and Problems

Exercise 3-1

Suppose ten hydrogen molecules and ten oxygen molecules are mixed. How many molecules of water could be formed? What would be left over?

Answer

Ten hydrogen molecules could combine with five oxygen molecules to make ten molecules of water. Five oxygen molecules would be left over.

Exercise 3-2

One million oxygen molecules react with sufficient hydrogen molecules to form water molecules. How many water molecules are formed? How many hydrogen molecules are required?

Answer

One million oxygen molecules could form two million water molecules, consuming two million hydrogen molecules in the process.

Exercise 3-3

How much heat is released when ten moles of hydrogen gas burn? One-tenth mole?

Answer

The burning of ten moles of H_2 will release

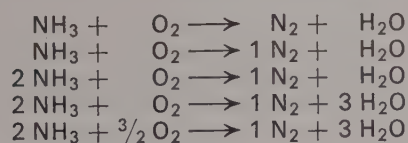
$$10(68) \text{ kcal} = 680 \text{ kcal}$$

The burning of $\frac{1}{10}$ mole of H_2 will release

$$\frac{1}{10}(68) \text{ kcal} = 6.8 \text{ kcal}$$

Exercise 3-4

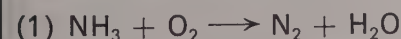
Ammonia gas, NH_3 , reacts with oxygen gas, O_2 , to give nitrogen gas, N_2 , and water, H_2O . Follow the logic of each step in balancing this reaction.



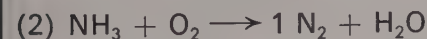
State briefly what was done in each step.

Answer

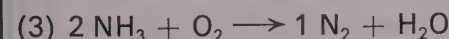
The student should follow the logic of conserving atoms: first, nitrogen atoms; then, hydrogen atoms; and, finally, oxygen atoms to reach the balanced equation.



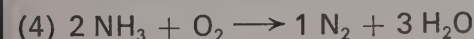
Write formulas for products and reactants.



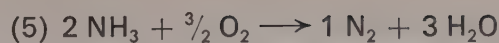
Choose one element to work on (N).



Arrange to conserve atoms of this element.



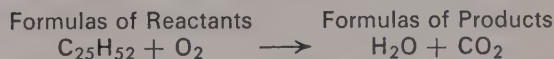
Do the same for another element (H), usually in a molecule containing the already balanced element.



Continue with the other elements (O).

Exercise 3-5

A paraffin candle burns in air to form water and carbon dioxide. Paraffin is made up of molecules of several sizes. We shall use the molecular formula $\text{C}_{25}\text{H}_{52}$ as representative of the molecules present.



Suppose one mole of paraffin is burned. We can write



We still have not determined the coefficient for O_2 . Since 76 O's are required for the products [$26 + (2 \times 25) = 76$], they must have been present in the reactants. Show that y must be 38:

**Answer**

To provide 76 oxygens, 38 molecules of O_2 are needed, each providing two atoms of oxygen.

Exercise 3-6

Show that 3.80 moles of oxygen are needed to burn 35.3 grams of paraffin by the reaction.

**Answer**

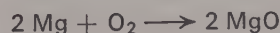
The molar mass of paraffin is

$$25(12.01) + 52(1.008) = 352.7 \text{ g/mole}$$

Hence 35.3 g of paraffin equals $35.3/353 = 0.100$ mole. But, by the reaction given, one mole of $\text{C}_{25}\text{H}_{52}$ reacts with 38 moles of O_2 ; hence 0.100 mole of $\text{C}_{25}\text{H}_{52}$ reacts with 3.80 moles of O_2 .

Exercise 3-7

How many moles of oxygen, O_2 , are required to produce 242 grams of magnesium oxide by the reaction

**Answer**

The molar mass of MgO is $24.3 + 16.00 = 40.3 \text{ g/mole}$.

$$242 \text{ g MgO} \times \frac{1 \text{ mole}}{40.3 \text{ g}} = 6.00 \text{ moles MgO}$$

By the equation, one mole of O_2 produces two moles of MgO .

$$6.00 \text{ moles } MgO \times \frac{1 \text{ mole } O_2}{2 \text{ moles } MgO} = 3.00 \text{ moles } O_2$$

Exercise 3-8

In Experiment 8 you determined the number of moles of silver chloride formed in the reaction of some sodium chloride with a known amount of silver nitrate. How many moles of sodium chloride reacted with the silver nitrate? Compare this with the number of moles of sodium chloride you added.

Answer

The following data are an example of what you might expect from the students:

moles $AgNO_3$ used = 0.030;

moles $AgCl$ produced = 0.031;

moles $NaCl$ reacted = 0.031;

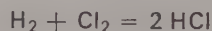
moles of $NaCl$ reacted = moles of $AgCl$ produced;

moles $NaCl$ added = 0.049;

0.018 mole of $NaCl$ in excess.

Problem 1

One volume of hydrogen gas combines with one volume of chlorine gas to give two volumes of hydrogen chloride gas. On the basis of many reactions, we have learned that the molecular formulas are H_2 for hydrogen, Cl_2 for chlorine, and HCl for hydrogen chloride. The reaction can be represented with this equation.



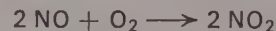
- According to this reaction, how many *molecules* of hydrogen chloride can be formed using one *molecule* of hydrogen?
- How many *moles* of hydrogen chloride can be formed using one *mole* of hydrogen?
- How many molecules of hydrogen chloride can be formed using four molecules of chlorine?
- How many moles of chlorine are required to produce eight moles of hydrogen chloride?

Answer

- Two molecules of HCl .
- Two moles of HCl .
- Eight molecules of HCl .
- Four moles of Cl_2 .

Problem 2

The reaction between nitric oxide, NO , and oxygen, O_2 , can be written



- How many molecules of nitrogen dioxide, NO_2 , can be formed using two molecules of nitric oxide?
- How many moles of nitric oxide are needed to give four moles of nitrogen dioxide?
- How many moles of oxygen atoms are there in one mole of oxygen molecules?
- How many moles of oxygen atoms are there in two moles of nitric oxide?
- How many moles of oxygen atoms are there in two moles of nitrogen dioxide?
- Use the answers to parts (c), (d), and (e) to verify that the reaction is written to conserve oxygen atoms.

Answer

- Two molecules of NO_2 .
- Four moles of NO_2 .
- Two moles of oxygen atoms.
- Two moles of oxygen atoms.
- Four moles of oxygen atoms.
- $2 + 2 = 4$.

Problem 3

Write the equation for the reaction between nitrogen and hydrogen to give ammonia. The molecular formulas are N_2 , H_2 , and NH_3 respectively.

- Verify that your equation conserves nitrogen atoms.
- Verify that your equation conserves hydrogen atoms.

Answer

- On the left, one molecule of N_2 contains two nitrogen atoms; on the right, two molecules of NH_3 also contain two nitrogen atoms.
- On the left, three molecules of H_2 contain six hydrogen atoms; on the right, two molecules of NH_3 also contain six hydrogen atoms.

Problem 4

Balance the equations for each of the following reactions. Begin on the basis of one mole of the underlined substance.

- $Li + \underline{Cl_2} \longrightarrow LiCl$
- $Na + \underline{Cl_2} \longrightarrow NaCl$
- $Na + \underline{F_2} \longrightarrow NaF$
- $\underline{Na} + Br_2 \longrightarrow NaBr$
- $\underline{O_2} + Cl_2 \longrightarrow Cl_2O$
- $O_2 + \underline{Cl_2} \longrightarrow Cl_2O$

Show that your answers to parts (e) and (f) contain the same information.

Answer

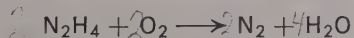
- (a) $2 \text{Li} + \text{Cl}_2 \longrightarrow 2 \text{LiCl}$
 (b) $2 \text{Na} + \text{Cl}_2 \longrightarrow 2 \text{NaCl}$
 (c) $2 \text{Na} + \text{F}_2 \longrightarrow 2 \text{NaF}$
 (d) $2 \text{Na} + \text{Br}_2 \longrightarrow 2 \text{NaBr}$
 (e) $\text{O}_2 + 2 \text{Cl}_2 \longrightarrow 2 \text{Cl}_2\text{O}$
 (f) $\frac{1}{2} \text{O}_2 + \text{Cl}_2 \longrightarrow \text{Cl}_2\text{O}$

Equation (e) indicates that one mole of oxygen reacts with two moles of chlorine to form two moles of Cl_2O . This implies that one-half mole of oxygen reacts with one mole of chlorine to form one mole of Cl_2O , which is exactly the information given by equation (f).

Problem 5

Balance the equations for each of the following reactions involving oxygen. Begin on the basis of one mole of the underlined substance.

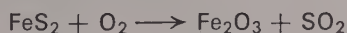
- (a) $\text{Ni} + \underline{\text{O}_2} \longrightarrow \text{NiO}$
 (b) $\underline{\text{Ni}} + \text{O}_2 \longrightarrow \text{NiO}$
 (c) $\text{Li} + \underline{\text{O}_2} \longrightarrow \text{Li}_2\text{O}$
 (d) With the rocket fuel hydrazine, N_2H_4 :



- (e) With the important copper ore, chalcocite, Cu_2S :



- (f) With the important iron ore, iron pyrites, FeS_2 . (This ore is sometimes referred to as "fool's gold" because of its bright golden luster.)



Answer

- (a) $2 \text{Ni} + \text{O}_2 \longrightarrow 2 \text{NiO}$
 (b) $\text{Ni} + \frac{1}{2} \text{O}_2 \longrightarrow \text{NiO}$
 (c) $4 \text{Li} + \text{O}_2 \longrightarrow 2 \text{Li}_2\text{O}$
 (d) $\text{N}_2\text{H}_4 + \text{O}_2 \longrightarrow \text{N}_2 + 2 \text{H}_2\text{O}$
 (e) $\text{Cu}_2\text{S} + \frac{3}{2} \text{O}_2 \longrightarrow \text{Cu}_2\text{O} + \text{SO}_2$
 (f) $2 \text{FeS}_2 + \frac{11}{2} \text{O}_2 \longrightarrow \text{Fe}_2\text{O}_3 + 4 \text{SO}_2$

Problem 6

If 3 grams of substance *A* combine with 4 grams of substance *B* to make 5 grams of substance *C* and some *D*, how many grams of *D* would you expect?

Answer

Assuming conservation of mass, we have

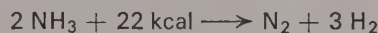
$$3 \text{ g} + 4 \text{ g} = 5 \text{ g} + D$$

$$7 \text{ g} - 5 \text{ g} = D$$

$$D = 2 \text{ g}$$

Problem 7

When ammonia is decomposed into nitrogen and hydrogen, the reaction absorbs heat energy. The equation can be written this way:



- (a) How many moles of nitrogen will be produced from two moles of ammonia?
 (b) How much heat energy would be absorbed during the production of one mole of nitrogen?
 (c) How much heat energy must be absorbed to produce nine moles of hydrogen?
 (d) Calculate the mass of two moles of ammonia. Compare that number to the sum of the masses of one mole of nitrogen and three moles of hydrogen.

Answer

- (a) One mole of nitrogen.
 (b) 22 kcal.
 (c) 66 kcal.
 (d) Two moles of NH_3 weigh

$$2[14.01 + 3(1.008)] = 2(17.034) \\ = 34.068 = 34.07 \text{ g}$$

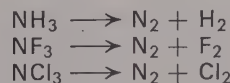
$$\text{One mole N}_2 \text{ weighs } 2(14.01) = 28.02 \text{ g}$$

$$\text{Three moles H}_2 \text{ weigh } 3[2(1.008)] \\ = 3 \times 2.016 = 6.048 \text{ g}$$

The total is 34.068 g or 34.07 g, the same as two moles of NH_3 .

Problem 8

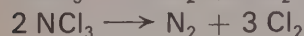
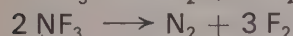
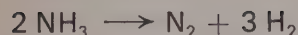
Balance the equations for the decomposition of ammonia, nitrogen trifluoride, and nitrogen trichloride into the elements. Base each equation on the formation of one mole of nitrogen.



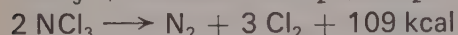
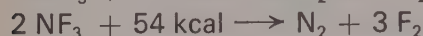
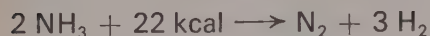
Rewrite these equations to include this information. Decomposition of ammonia and nitrogen trifluoride are *endothermic* reactions, 22 kcal and 54 kcal per mole of nitrogen, respectively. The decomposition of nitrogen trichloride is *exothermic*, 109 kcal per mole of nitrogen. Which of these three compounds would you expect to be dangerously explosive?

Answer

First



then



Nitrogen trichloride, NCl_3 , is the compound most likely to be explosive because of the large energy release on decomposition. (It *is* explosive and it is *extremely dangerous*.)

Problem 9

In the manufacture of nitric acid, HNO_3 , nitrogen dioxide reacts with water according to this equation:



- Verify that the equation conserves oxygen atoms.
- How many molecules of nitrogen dioxide are required to form 25 molecules of nitric oxide?
- How many moles of nitric oxide are formed from 0.60 mole of nitrogen dioxide?

Answer

- 3 NO_2 molecules
contain 6 oxygen atoms

1 H_2O molecule
contains 1 oxygen atom

Reactant molecules
contain 7 oxygen atoms

2 HNO_3 molecules
contain 6 oxygen atoms

1 NO molecule
contains 1 oxygen atom

Product molecules
contain 7 oxygen atoms
(same as in reactants)
- Three molecules of NO_2 form one molecule of NO . Hence 3×25 molecules of NO_2 form 25 molecules of NO ; that is, 75 molecules of NO_2 are required.
- Three moles of NO_2 form one mole of NO . Hence 0.60 mole of NO_2 forms $0.60/3 = 0.20$ mole of NO .

Problem 10

One step in the manufacture of sulfuric acid is the burning of sulfur, S_8 , in air to form a colorless gas, SO_2 , sulfur dioxide. On the basis of this information:

- Write the balanced equation for this reaction.
- Interpret the equation in terms of molecules.
- Interpret the equation in terms of words.
- How many moles of sulfur dioxide can be produced from two moles of sulfur?

Answer

- $\text{S}_8 + 8 \text{O}_2 = 8 \text{SO}_2$.
- One molecule of S_8 reacts with eight molecules of O_2 to form eight molecules of SO_2 .
- Same as (b).
- Sixteen moles of SO_2 .

Problem 11

When iron rusts, it combines with oxygen of the air to form iron oxide, Fe_2O_3 . Which of the following statements is FALSE?

- The equation is $3 \text{O}_2 + 4 \text{Fe} \longrightarrow 2 \text{Fe}_2\text{O}_3$
- There are five atoms represented by the formula Fe_2O_3 .
- Oxygen gas is triatomic.
- The mass of the reactants equals the mass of the products.
- Atoms are conserved.

Answer

Part (c) is false. Oxygen gas is diatomic.

Problem 12

Chlorine, Cl_2 , is one of the most important industrial chemicals that we know. Each year many tons of chlorine are produced by the electrolysis of sodium chloride. Most of this chlorine is used to purify water supplies or to bleach paper and cloth. The other product of this electrolysis is metallic sodium.

- Write a balanced equation for this electrolytic reaction.
- How many kilograms of sodium chloride are required to make 1.00×10^3 kilograms of chlorine?

Answer

- $2 \text{NaCl} \longrightarrow 2 \text{Na} + \text{Cl}_2$
- $$\left(\frac{1.00 \times 10^6 \text{ g Cl}_2}{71 \text{ g/mole Cl}_2} \right) \left(\frac{2 \text{ moles NaCl}}{1 \text{ mole Cl}_2} \right)$$

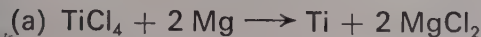
$$\times \left(\frac{58.5 \text{ g NaCl}}{\text{mole NaCl}} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right)$$

$$= 1650 \text{ kg NaCl needed}$$

Problem 13

Large amounts of the very important metal titanium, Ti, are made by reacting titanium tetrachloride with magnesium metal. Titanium metal and magnesium chloride, MgCl_2 , are produced.

- Write the balanced equation for the reaction.
- How many kilograms of magnesium are required to produce one kilogram of titanium?

Answer

$$(b) \left(\frac{1000 \text{ g Ti}}{50 \text{ g/mole Ti}} \right) \left(\frac{2 \text{ moles Mg}}{\text{mole Ti}} \right) \times \left(\frac{24.3 \text{ g Mg}}{\text{mole Mg}} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 0.97 \text{ kg Mg required}$$

Problem 14

Copper wire reacts with silver nitrate solution to produce silver metal and a solution of copper nitrate, $\text{Cu}(\text{NO}_3)_2$.

- Write a balanced equation for the reaction.
- How many grams of metallic silver would be produced if 2.37 g of copper reacted?

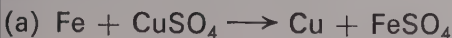
Answer

$$(b) \left(\frac{2.37 \text{ g Cu}}{63.5 \text{ g/mole Cu}} \right) \left(\frac{2 \text{ moles Ag}}{\text{mole Cu}} \right) \times \left(\frac{108 \text{ g Ag}}{\text{mole Ag}} \right) = 8.0 \text{ g Ag produced}$$

Problem 15

When iron filings react with a copper sulfate solution, metallic copper and a solution of iron sulfate, FeSO_4 , are produced.

- Write a balanced equation for the reaction.
- How many moles of copper would be produced if 2.45 g of iron react with an excess of copper sulfate solution?
- How many grams of copper would be produced?

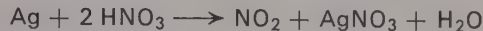
Answer

$$(b) \left(\frac{2.45 \text{ g Fe}}{55.8 \text{ g/mole Fe}} \right) \left(\frac{1 \text{ mole Cu}}{\text{mole Fe}} \right) = 0.0440 \text{ mole Cu}$$

$$(c) (0.0440 \text{ mole Cu})(63.5 \text{ g/mole Cu}) = 2.79 \text{ g Cu}$$

Problem 16

Silver reacts with nitric acid as indicated by the equation



- How many grams of nitric acid would be required to react with 5.00 g of silver?
- How many grams of water would be formed?
- How many grams of nitrogen dioxide would be produced?

Answer

$$(a) \left(\frac{5.00 \text{ g Ag}}{107.9 \text{ g/mole Ag}} \right) \left(\frac{2 \text{ moles HNO}_3}{\text{mole Ag}} \right) \times \left(\frac{63.02 \text{ g}}{\text{mole HNO}_3} \right) = 5.85 \text{ g HNO}_3 \text{ needed}$$

$$(b) \left(\frac{5.00 \text{ g Ag}}{107.9 \text{ g/mole Ag}} \right) \left(\frac{1 \text{ mole H}_2\text{O}}{\text{mole Ag}} \right) \times \left(\frac{18.0 \text{ g}}{\text{mole H}_2\text{O}} \right) = 0.835 \text{ g H}_2\text{O formed}$$

$$(c) \left(\frac{5.00 \text{ g Ag}}{107.9 \text{ g/mole Ag}} \right) \left(\frac{1 \text{ mole NO}_2}{\text{mole Ag}} \right) \times \left(\frac{46.0 \text{ g}}{\text{mole NO}_2} \right) = 2.13 \text{ g NO}_2 \text{ produced}$$

Problem 17

Hydrated copper sulfate, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, decomposes when heated, to form anhydrous copper sulfate, CuSO_4 , and water.

- Write a balanced equation for the reaction.
- How many grams of water would form if 5.00 g of the hydrate are heated?
- How much of the anhydrous copper sulfate would be produced if 5.00 g of the hydrate is heated?

Answer

$$(b) \left(\frac{5.00 \text{ g hydrate}}{249.6 \text{ g/mole hydrate}} \right) \left(\frac{5 \text{ moles H}_2\text{O}}{\text{mole hydrate}} \right) \times \left(\frac{18.0 \text{ g}}{\text{mole H}_2\text{O}} \right) = 1.80 \text{ g H}_2\text{O formed}$$

$$(c) \left(\frac{5.00 \text{ g hydrate}}{249.6 \text{ g/mole hydrate}} \right) \left(\frac{1 \text{ mole CuSO}_4}{\text{mole hydrate}} \right) \times \left(\frac{159.7 \text{ g}}{\text{mole CuSO}_4} \right) = 3.20 \text{ g CuSO}_4 \text{ produced}$$

Problem 18

Large amounts of SO_2 needed to make H_2SO_4 are obtained by the reaction shown in Problem 5 (f). The Fe_2O_3 produced is also useful. It can be used in blast furnaces to produce iron (the compound FeS_2 cannot be used in blast furnaces).

- How many kilograms of FeS_2 are needed to produce 128 kilograms of SO_2 ?
- Does the Fe_2O_3 weigh more or less than the FeS_2 from which it is made?

Answer

$$\begin{aligned} \text{(a)} \quad & \left(\frac{128,000 \text{ g SO}_2}{64.1 \text{ g/mole SO}_2} \right) \left(\frac{1 \text{ mole FeS}_2}{2 \text{ moles SO}_2} \right) \\ & \times \left(\frac{120.0 \text{ g}}{\text{mole FeS}_2} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) \\ & = 120 \text{ or } 1.20 \times 10^2 \text{ kg FeS}_2 \text{ required} \end{aligned}$$

- Many students will answer by working out the mass of Fe_2O_3 in a way similar to part (a). That is correct, but a shorter way is to compare masses of one mole Fe_2O_3 (159.7 g) and two moles of FeS_2 (240 g). The Fe_2O_3 weighs less than the FeS_2 from which it is formed.

Problem 19

Use the equation obtained in Problem 10 to answer these questions.

- How many kilograms of S_8 are needed to produce 641 kilograms of SO_2 ?
- SO_2 can be burned to form SO_3 . How many kilograms of SO_2 are needed to produce 801 kilograms of SO_3 ?
- SO_3 reacts with water to form H_2SO_4 . How many kilograms of sulfur are needed to produce 981 kilograms of sulfuric acid?

Answer

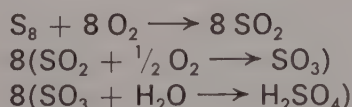
$$\begin{aligned} \text{(a)} \quad & \left(\frac{641,000 \text{ g SO}_2}{64.1 \text{ g/mole SO}_2} \right) \left(\frac{1 \text{ mole S}_8}{8 \text{ moles SO}_2} \right) \\ & \times \left(\frac{256.8 \text{ g}}{\text{mole S}_8} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 321 \text{ kg S}_8 \text{ required} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad & \text{SO}_2 + \frac{1}{2} \text{O}_2 \longrightarrow \text{SO}_3 \\ & \left(\frac{801,000 \text{ g SO}_3}{80.1 \text{ g/mole SO}_3} \right) \left(\frac{1 \text{ mole SO}_2}{\text{mole SO}_3} \right) \\ & \times \left(\frac{64.1 \text{ g}}{\text{mole SO}_2} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 641 \text{ kg SO}_2 \text{ needed} \end{aligned}$$



$$\begin{aligned} & \left(\frac{981,000 \text{ g H}_2\text{SO}_4}{98.1 \text{ g/mole H}_2\text{SO}_4} \right) \left(\frac{1 \text{ mole S}_8}{8 \text{ moles H}_2\text{SO}_4} \right) \\ & \times \left(\frac{256.5 \text{ g}}{\text{mole S}_8} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 321 \text{ kg S}_8 \text{ required} \end{aligned}$$

Students may have trouble getting the factor (1 mole S_8 /moles H_2SO_4). If the three equations are written beneath one another, the relation is clearer.



Problem 20

Graphite is one form of carbon, C. It can be burned in air to produce carbon dioxide.

- Write the equation for the reaction.
- If one mole of graphite is burned, how many moles of carbon dioxide are produced? What is the mass in grams for this amount of carbon dioxide?
- If five moles of graphite are burned in a vessel containing 10 moles of oxygen gas, what is the maximum number of moles of carbon dioxide that could be produced?

Answer

- $\text{C} + \text{O}_2 = \text{CO}_2$
- One mole of C gives one mole of CO_2 , which weighs 44.01 g.
- Five moles of C give five moles of CO_2 . This would be mixed with five moles of unused O_2 .

Problem 21

If a piece of sodium metal is lowered into a bottle of chlorine gas, a reaction takes place. Sodium chloride, table salt, is formed.

- Write the equation for the reaction.
- How many moles of sodium chloride could be formed using one mole of sodium?
- How many moles of sodium chloride could be formed using 2.30 grams of sodium?

Answer

- $2 \text{Na} + \text{Cl}_2 = 2 \text{NaCl}$
- One mole of Na produces one mole of NaCl.
- 2.30 g of Na is $2.30/23.0 = 0.100$ mole; this amount will produce 0.100 mole of NaCl.

Problem 22

Methane, the principal constituent of natural gas, has the formula CH_4 . When it is burned in air, the combustion products are carbon dioxide and water.

- Write the equation for the combustion of methane.
- How many moles of water could be formed using one mole of methane?
- How many moles of water would be produced when 4.0 grams of methane are burned?

Answer

- $\text{CH}_4 + 2 \text{O}_2 = \text{CO}_2 + 2 \text{H}_2\text{O}$
- One mole of CH_4 produces two moles of H_2O .
- $4.0 \text{ g} = (4.0/16.0) \text{ mole of } \text{CH}_4 = 0.25 \text{ mole of } \text{CH}_4$, which yields 0.50 mole of H_2O .

Problem 23

If potassium chlorate, KClO_3 , is heated gently, the crystals will melt. When the temperature gets high enough, potassium chlorate decomposes to give oxygen gas and potassium chloride, KCl .

- Write the equation for this decomposition.
- How many moles of KClO_3 are needed to give 1.5 moles of oxygen?
- How many moles of KCl would be formed when 0.33 mole of KClO_3 decomposes?
- How many moles of oxygen would be produced from 122.6 grams of KClO_3 ?

Answer

- $2 \text{KClO}_3 = 3 \text{O}_2 + 2 \text{KCl}$
- One mole of KClO_3 produces 1.5 moles of O_2 .
- One-third mole of KClO_3 gives $\frac{1}{3}$ mole of KCl .
- 122.6 g of KClO_3 is one mole. One mole of KClO_3 produces 1.5 moles of O_2 .

Problem 24

One gallon of gasoline can be considered to be about 25 moles of octane, C_8H_{18} .

- How many moles of oxygen must be used to burn one gallon of gasoline, forming carbon dioxide and water?
- How many moles of carbon dioxide are formed? How many kilograms?
- How much carbon dioxide is released into the atmosphere when 10 gallons of gasoline are used in an automobile? Express your answer in pounds as well as kilograms. (1 kilogram = 2.2 pounds.)

Answer

- $\text{C}_8\text{H}_{18} + \frac{25}{2} \text{O}_2(\text{g}) \longrightarrow 8 \text{CO}_2(\text{g}) + 9 \text{H}_2\text{O}(\text{g})$
One mole of C_8H_{18} requires $\frac{25}{2}$ or 12.5 moles of O_2 . Twenty-five moles of C_8H_{18} require $25(\frac{25}{2}) = 312$ moles of $\text{O}_2 = 3.1 \times 10^2$ moles of O_2 .
- One mole of C_8H_{18} forms eight moles of CO_2 . Twenty-five moles of C_8H_{18} form 200 moles of $\text{CO}_2 = 2.0 \times 10^2$ moles of CO_2 .
One mole of CO_2 weighs 44 g.
200 moles of CO_2 weigh $8800 \text{ g} = 8.8 \text{ kg}$.
- 194 lb.

Problem 25

Iron burns in air to form a black solid oxide, Fe_3O_4 .

- Write the equation for the reaction.
- How many moles of oxygen are needed to react with one mole of iron?
- How many grams of oxygen would this be?
- Can a piece of iron weighing 5.6 grams burn completely to Fe_3O_4 in a vessel containing 0.05 mole of O_2 ?

Answer

- $3 \text{Fe} + 2 \text{O}_2 = \text{Fe}_3\text{O}_4$
- Three moles of Fe need two moles O_2 ; therefore one mole of Fe requires $\frac{2}{3}$ mole of O_2 .
- One mole of O_2 weighs 32.00 g; thus $\frac{2}{3}$ mole weighs $(\frac{2}{3})(32.00) = 21.33 \text{ g}$.
- No, since 5.6 g Fe equals 0.10 mole. This requires $(\frac{2}{3})(0.1) = 0.066$ mole O_2 . Only 0.05 mole is present; hence the iron cannot be completely converted to Fe_3O_4 .

Problem 26

The reaction in Problem 9 relates to the manufacture of nitric acid.

- How many grams of nitric acid are formed from one mole of nitrogen dioxide, according to the equation in Problem 9?
- How many more grams of nitric acid could be made if the nitric oxide, NO , formed could be completely converted to nitric acid?

Answer

- Three moles of nitrogen dioxide form two moles of nitric acid. Therefore one mole of nitrogen dioxide forms $\frac{2}{3}$ mole of nitric acid. The molar mass of HNO_3 is 63.0 g. Hence $\frac{2}{3}$ mole of HNO_3 weighs 42.0 g.

- (b) For every two moles of HNO_3 formed, one mole of NO is also formed. Hence the yield can be increased by 50% if the NO can be converted completely to HNO_3 . Thus an additional $42.0/2 = 21.0$ g can be formed.

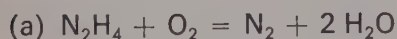
Alternatively, one mole of NO_2 gives $\frac{1}{3}$ mole of NO . If this $\frac{1}{3}$ mole of NO is converted to $\frac{1}{3}$ mole of HNO_3 , we obtain $(\frac{1}{3})(63.0) = 21.0$ g additional HNO_3 .

Problem 27

Hydrazine, N_2H_4 , can be burned with oxygen to provide energy for rocket propulsion. The energy released is 150 kcal per mole of hydrazine burned.

- (a) How much energy is released if 10.0 kg of hydrazine fuel are burned? Look at Problem 5 (d) for the reaction of hydrazine with oxygen.
 (b) Compare the energy that would be released if the same mass of hydrogen, 10.0 kg, is burned as fuel instead (see Section 3-1).

Answer



One mole of N_2H_4 weighs 32.0 g. Hence,

$$10.0 \text{ kg} = 10.0 \times 10^3 \text{ g}$$

$$\frac{10.0 \times 10^3}{32.0} = 313 \text{ moles } \text{N}_2\text{H}_4$$

Heat released equals

$$(150 \text{ kcal/mole})(313 \text{ moles}) = 4.70 \times 10^4 \text{ kcal}$$

- (b) One mole of H_2 weighs 2.016 g. Hence,

$$10.0 \text{ kg} = 10.0 \times 10^3 \text{ g}$$

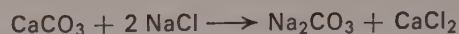
$$\frac{10.0 \times 10^3}{2.02} = 4.95 \times 10^3 \text{ moles } \text{H}_2$$

Heat released equals

$$(68.0 \text{ kcal/mole})(4.95 \times 10^3 \text{ moles}) = 33.4 \times 10^4 \text{ kcal}$$

Problem 28

Although sodium carbonate is needed in the manufacture of glass, very little sodium carbonate is found in nature. It is made using two very abundant chemicals, calcium carbonate (limestone) and sodium chloride. The process involves several steps. The overall reaction can be expressed this way:



- (a) How many grams of sodium chloride react with 1.00 kg of calcium carbonate?
 (b) How many grams of sodium carbonate are produced?

Answer

$$(a) \left(\frac{1000 \text{ g } \text{CaCO}_3}{100 \text{ g/mole}} \right) \left(\frac{2 \text{ moles NaCl}}{\text{mole } \text{CaCO}_3} \right) \times \left(\frac{58.5 \text{ g}}{\text{mole NaCl}} \right) = 1170 \text{ g NaCl used}$$

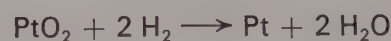
$$(b) \left(\frac{1000 \text{ g } \text{CaCO}_3}{100 \text{ g/mole } \text{CaCO}_3} \right) \left(\frac{1 \text{ mole } \text{Na}_2\text{CO}_3}{\text{mole } \text{CaCO}_3} \right) \times \left(\frac{106 \text{ g}}{\text{mole } \text{Na}_2\text{CO}_3} \right) = 1060 \text{ g } \text{Na}_2\text{CO}_3 \text{ made}$$

Problem 29

A substance used in manufacturing gasoline consists of finely divided platinum supported on an inert solid. Suppose that the platinum is formed by the high temperature reaction between platinum dioxide, PtO_2 , and hydrogen gas to form platinum metal and water.

- (a) How many grams of hydrogen are needed to produce 1.0 gram of platinum metal?
 (b) How many moles of water are produced at the same time? How many grams of water?

Answer



$$(a) \left(\frac{1.0 \text{ g Pt}}{195 \text{ g/mole Pt}} \right) \left(\frac{2 \text{ moles } \text{H}_2}{\text{mole Pt}} \right) \left(\frac{2.0 \text{ g}}{\text{mole } \text{H}_2} \right) = 0.020 \text{ g } \text{H}_2 \text{ required}$$

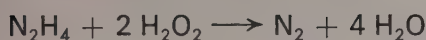
$$(b) \left(\frac{1.0 \text{ g Pt}}{195 \text{ g/mole Pt}} \right) \left(\frac{2 \text{ moles } \text{H}_2\text{O}}{\text{mole Pt}} \right) = 0.010 \text{ mole } \text{H}_2\text{O}$$

$$(0.010 \text{ mole})(18.0 \text{ g/mole } \text{H}_2\text{O}) = 0.18 \text{ g } \text{H}_2\text{O}$$

Problem 30

Hydrazine, N_2H_4 , and hydrogen peroxide, H_2O_2 , are used together as a rocket fuel. The products of the reaction are nitrogen and water. How many grams of hydrogen peroxide are needed per 1.00×10^3 grams of hydrazine carried by the rocket?

Answer



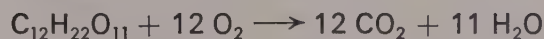
$$\left(\frac{1.00 \times 10^3 \text{ N}_2\text{H}_4}{32.1 \text{ g N}_2\text{H}_4/\text{mole}} \right) \left(\frac{2 \text{ moles H}_2\text{O}_2}{\text{mole N}_2\text{H}_4} \right) \times \left(\frac{34.0 \text{ g H}_2\text{O}_2}{\text{mole}} \right) = 2.12 \times 10^3 \text{ g H}_2\text{O}_2$$

Problem 31

The hourly energy requirements of an astronaut can be satisfied by the energy released when 34 grams of sucrose

are burned in his body. How many grams of oxygen would need to be carried in a space capsule to meet this requirement? The formula of sucrose is $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. Assume that the products of the reaction are carbon dioxide and water.

Answer



$$\left(\frac{34 \text{ g sugar}}{342.3 \text{ g/mole sugar}} \right) \left(\frac{12 \text{ moles O}_2}{\text{mole sugar}} \right) \times \left(\frac{32 \text{ g}}{\text{mole O}_2} \right) = 38 \text{ g O}_2 \text{ needed}$$

Suggested Quiz Questions

These suggested questions are designed for a one-period open-book test. There are more than enough; hence some selection is required.

1. Balance the following:

- (1) $\text{Al} + \text{O}_2 \rightleftharpoons \text{Al}_2\text{O}_3$
- (2) $\text{Cu} + \text{S}_8 \rightleftharpoons \text{CuS}$
- (3) $\text{C}_2\text{H}_5\text{OH} + \text{O}_2 \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O}$
- (4) $\text{FeS} + \text{O}_2 \rightleftharpoons \text{Fe}_2\text{O}_3 + \text{SO}_2$

Answer

- (1) $4 \text{ Al} + 3 \text{ O}_2 = 2 \text{ Al}_2\text{O}_3$
 $2 \text{ Al} + 1\frac{1}{2} \text{ O}_2 = \text{Al}_2\text{O}_3$
- (2) $8 \text{ Cu} + \text{S}_8 = 8 \text{ CuS}$
- (3) $\text{C}_2\text{H}_5\text{OH} + 3 \text{ O}_2 = 2 \text{ CO}_2 + 3 \text{ H}_2\text{O}$
- (4) $2 \text{ FeS} + 7\frac{1}{2} \text{ O}_2 = \text{Fe}_2\text{O}_3 + 2 \text{ SO}_2$

2. One mole of nitrogen gas, N_2 , reacts with three moles of hydrogen gas, H_2 , to produce two moles of ammonia gas, NH_3 .

- (1) Write the equation for the reaction.
- (2) If all the gases were measured at the same temperature and pressure, how would the volumes of the gases compare?
- (3) What mass of ammonia is produced by two moles of nitrogen?

Answer

- (1) $\text{N}_2 + 3 \text{ H}_2 = 2 \text{ NH}_3$
- (2) One volume of N_2 to three of H_2 , giving two of NH_3 .

(3) Two moles of N_2 give four moles ammonia:

$$4(17 \text{ g/mole}) = 78 \text{ g NH}_3$$

3. Phosphorus, P_4 , burns in air to form the oxide, P_4O_{10} .

- (1) Write the equation for this reaction.
- (2) How many moles of oxygen are required to burn 2.0 moles of phosphorus, P_4 ?
- (3) How many grams of P_4O_{10} would be produced when 0.20 mole of phosphorus, P_4 , is burned?

Answer

- (1) $\text{P}_4 + 5 \text{ O}_2 = \text{P}_4\text{O}_{10}$
- (2) Ten moles of O_2 are needed.
- (3) 0.20 mole P_4 would give 0.20 mole P_4O_{10} .

$$0.20 \text{ mole} \times \frac{284 \text{ g}}{\text{mole}} = 56.8 \text{ g P}_4\text{O}_{10}$$

or

$$57 \text{ g P}_4\text{O}_{10}$$

4. The following equation represents the combustion of acetylene, C_2H_2 .



- (1) What specific information does this equation impart?
- (2) Assume that 0.5 mole of C_2H_2 is available

for combustion. How many moles of each product would form? How much heat would be evolved?

- (3) How many moles of gaseous oxygen will react with 1 kg of C_2H_2 ?

Answer

- (1) The equation reveals that one mole of acetylene reacts with $2\frac{1}{2}$ moles of oxygen to form two moles of carbon dioxide and one mole of water. The reaction liberates 310 kcals of heat per mole of acetylene. It also shows the ratio of molecules reacting and forming.
- (2) If 0.5 mole of acetylene were available, one mole of CO_2 and 0.5 mole of H_2O would be formed. The heat evolved would be (310 kcals/mole) $\times$ 0.5 mole = 155 kcals.
- (3) 1 kg = 1000 g;

$$\frac{1000 \text{ g}}{26 \text{ g/mole } C_2H_2} = 38.5 \text{ moles } C_2H_2$$

This would require

$$38.5 \times 2\frac{1}{2} = 96.3 \text{ moles } O_2$$

5. Consider these statements about a chemical equation. Which are FALSE?

- (1) Mass is conserved.
- (2) Molecules are conserved.
- (3) Atoms are conserved.
- (4) Moles are conserved.
- (5) There is only one set of numbers that can represent the proper ratio of reacting molecules.

Answer: 2, 4, and 5 are false.

6. Balance the following:

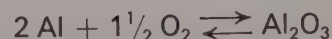
- (1) $CO + O_2 \rightleftharpoons CO_2$
- (2) $Zn + O_2 \rightleftharpoons ZnO$
- (3) $P_4 + S_8 \rightleftharpoons P_2S_5$
- (4) $HgO \rightleftharpoons Hg + O_2$
- (5) $C_2H_6 + O_2 \rightleftharpoons CO_2 + H_2O$

Answer

- (1) $2 CO + O_2 = 2 CO_2$
- (2) $2 Zn + O_2 = 2 ZnO$

- (3) $4 P_4 + 5 S_8 = 8 P_2S_5$
- (4) $2 HgO = 2 Hg + O_2$
- (5) $C_2H_6 + 3\frac{1}{2} O_2 = 2 CO_2 + 3 H_2O$

7. The equation for aluminum burning in air is



- (1) How many moles of oxygen are required to react with 0.25 mole of aluminum?
- (2) How many grams of Al_2O_3 are formed from 0.25 mole Al?
- (3) Suppose one mole of Al and one mole of O_2 react. Which reactant remains. How many moles?

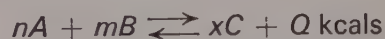
Answer

- (1) Two moles of Al require 1.5 moles O_2 .
1 mole Al requires $1.5/2 = 0.75$ mole.
0.25 mole Al needs $0.75/4 = 0.187$ mole.
- (2) One mole of Al_2O_3 weighs 102 g.

$$102 \text{ g} \times 0.25/2 = 12.8 \text{ g } Al_2O_3$$

- (3) Oxygen remains; $\frac{1}{4}$ mole.

8. Given the equation



in which A, B, and C are each a pure gaseous substance:

- (1) Does this equation illustrate a "phase change" or a "chemical change"? Explain.
- (2) Must $n + m = x$? Explain.
- (3) Assume the molar mass of A to be 24 and of C to be 72. In terms of n and x, express the number of moles of A required to form 100 grams of C.

Answer

- (1) This represents a "chemical change." Note that each of the substances is in the gas phase. Since C represents a new species, a chemical change is represented.
- (2) No. An equation always conserves

atoms, but not necessarily molecules. Since we do not know the composition of A , B , and C , then $n + m$ does not necessarily equal x .

$$(3) \text{ Moles of } A = \left(\frac{100 \text{ g}}{72 \text{ g/mole } C} \right) \times \left(\frac{n \text{ moles } A}{x \text{ moles } C} \right) = \frac{100 n}{72 x}.$$

9. Consider the equation $4D + 3E \rightleftharpoons D_4E_3$.

(1) Assume 0.1 mole of D_4E_3 is formed in a

reaction. What is the *total* number of moles of D and E consumed?

(2) Assume that 1.2 moles of E react completely with D . What is the *total* number of moles in the reaction?

Answer

(1) 0.7 mole.

(2) $\frac{4}{3}D + E = \frac{1}{3}D_4E_3$. Therefore 1.2 E requires $(\frac{4}{3})(1.2)$ moles D and gives $(\frac{1}{3})(1.2)$ mole D_4E_3 . Total moles are $1.2 + 1.6 + 0.4 = 3.2$.

The Gas Phase



Intent and Approach

This chapter opens with three sections on regularities of gas behavior. These are to strengthen the particle model, introduce partial pressure, and establish absolute temperature. From the connection between temperature, kinetic energy, and particle velocity it is a short step to the distribution of velocities.

These ideas are important: in this chapter, for

understanding gases; and later, for understanding liquids, rates of reaction, and equilibria. Here, as in earlier chapters, specific "gas law" formulas are not presented. Their intent is that a student who understands the fairly simple basis of the absolute temperature scale will have no trouble making a temperature correction. The reverse is not necessarily true.

Outline

The P - V relation is used to introduce partial pressure (4-1). The total gas pressure depends on the *number* of particles, not the kind. In a mixture each gas contributes independently and in proportion to the number of molecules present.

Experimental data on gas volume versus temperature show a new regularity and lead to absolute temperature (4-2).

Pressure and temperature are seen to be related

(4-3) and lead into the meaning of temperature (4-4) as translational motion of molecules.

The kinetic theory is reviewed briefly (4-5) and a method of measuring molecular velocity described (4-6). The distribution curve of velocity and its variation with temperature comes up here.

Molar volume (4-7) is used to show that gas particles are quite far apart on a molecular scale.

New Concepts

1. The V - T and P - T relations.
2. Partial pressure: each gas in a mixture contributes pressure independently of the others.
3. Relationship between temperature of gases

- and the kinetic energy of the molecules.
4. Absolute zero.
5. Distribution of molecular velocities.

SCHEDULE AND RELATED MATERIAL

Suggested Time : 8 days

Text Section	Topic and Other Work	Exercises	Problems		
			Easy	Medium	Hard
	Expt. 10. Temperature—Volume Relation				
4-1	<i>P-V</i>	1, 2		3, 4, 6	7, 8, 28, 29
4-2	<i>V-T</i> Note 1	3	1, 12	2, 11, 14	18
	Demo. 10. Molecular Motion				
4-3	<i>P-T</i>		24–27	17, 31	19, 20, 30
	Demo. 11. Pressure-Temperature Relation				
4-4	The Meaning of Temperature	4	10	21	22
	Film: Gas Pressure and Molecular Collisions				
4-5	Kinetic Theory		5, 9		
4-6	Molecular Velocities				
	Demo. 12. Diffusion Rate Increases with Temperature				
4-7	Molar Volume	5	13	15, 16	23
	Demo. 15. Liquid to Gas Change of Phase				
4-8	Review				

Note 1. Expt. 11, The Reaction of Magnesium with Hydrochloric Acid, can be done any time after Section 4-1. See p. 58 of the Laboratory Guide. Demonstrations 13 and 14 are related to this experiment.

Development

Expt. 10, TEMPERATURE-VOLUME RELATION

fits here. See p. 49 in the Laboratory Guide.

4-1 Pressure-Volume Regularity

The *P-V* relation found in Chapter 2 is used to introduce partial pressure. The kinetic particle model of gases makes partial pressure easier to understand. The logic goes this way. Experimental evidence shows that in mixtures of gases the total pressure is equal to the sum of the individual pressures due to each individual gaseous component. The pressure caused by any

single component of the mixture is proportional to the number of particles of that component. Thus the ratio of the number of its molecules to the total number of molecules present gives the fraction of the pressure caused by that component.

Demonstration 8 can be used here or in the next section.

4-2 Volume-Temperature Regularity

The effect of temperature changes on gas volume and the subsequent development of an absolute temperature scale can best be demonstrated by using some technique such as the one shown in this section of the Textbook.

The curve obtained can then be extrapolated to show absolute zero is in the vicinity of -273°C . A comparison of absolute (Kelvin) and Celsius temperature scales fits in at this point. (Do not spend time on Celsius-Fahrenheit conversions.) Compare some standard reference points on the two scales. The student should be able to convert $^{\circ}\text{C}$ to $^{\circ}\text{K}$ and the reverse.

Note that Table 4-1 in the Textbook also gives molar volume at five temperatures. This is a good place to point out that 22.4 liter/mole is *not* a fundamental constant. It just happens to be the volume of a certain amount of gas at some arbitrary conditions (STP).

Demo. 10, MOLECULAR MOTION,

fits here. See p. 52 in the Laboratory Guide.

4-3 Pressure-Temperature Regularity

The two preceding Sections have shown that P is related to V and that V is related to T . It is no surprise that P is related to T . This section verifies that connection.

Demo. 11, PRESSURE-TEMPERATURE RELATION,

fits here. See p. 54 in the Laboratory Guide.

4-4 The Meaning of Temperature

The first concept of this Section deals with how a thermometer works. You might open this subject with that question. The most common answer will be that "heat flows from the hot to the cold object." A further question asking how does it flow will get you to the point of using the kinetic model. Most students do not think of the molecular motion present in all the substances around them. This is a good place to emphasize it.

From this section the student should also get the idea that the temperature of a gas is a measure of the average kinetic energy of its molecules. It will then follow that the molecules of all gases

at the same temperature must have the same average kinetic energy. For this to be possible, the lighter molecules of gases with low molar mass must move faster, and the heavier molecules of the high molar mass gases must move slower in order for the net "push" or force per unit area (pressure) to be the same for each. Exercise 4-4 and, later, Table 4-3 bring out the point.

Film: GAS PRESSURE AND MOLECULAR COLLISIONS

fits here. See p. 67.

4-5 Kinetic Theory of Gases**4-6 Molecular Velocities**

In this section the experimental evidence for the distribution of kinetic energies of molecules is shown. The principles of the experiment, not the details of the apparatus, are important. The result given in Textbook *Figure 4-8 is vital*. Equally crucial is the change of this distribution with temperature (Figure 4-10 in the Textbook). Make sure the student understands this curve. In particular, he needs to know that relatively small changes in temperature make large changes in the fraction of high-energy molecules. In Chapter 12 we will apply this knowledge to explaining the rates of reactions.

The number of collisions a single molecule makes in one second, about 10^9 or one billion, is derived from the kinetic theory by means of the "mean free path." Standard physical chemistry texts show this derivation, and some mathematically inclined student may enjoy working on it further.

Demo. 12, DIFFUSION RATE INCREASES WITH TEMPERATURE,

fits here. See p. 56 in the Laboratory Guide.

4-7 Molar Volumes

The relatively large volumes occupied by substances in the gas phase are made clear to the student by comparing the density of ammonia in each of its three physical states. The relative volume occupied by one mole of ammonia is calculated for each state. The ratio between the gaseous volume and the liquid volume of the same mass is about 1000/1. Point out that changes in volume and density accompanying changes in temperature and pressure are very small for solids and liquids in comparison to the changes for gases. In fact, the kinetic model is a "good" model partly because of the great distance between molecules that this volume ratio reflects.

A model that treats gas molecules as ideal, hard, perfectly elastic spheres obeying the physical laws for such systems is an extremely useful one. Students should be reminded that its usefulness stems from its success in explaining the behavior of many gases over a wide range of temperatures and pressures. Most gases behave in accordance with this model when not near their boiling temperature and at low pressures. Refer to the background material for a more advanced treatment of corrective factors that must be applied to systems which depart from "ideality"; i.e., systems that do not closely follow the predictions based on the model.

Problem 4-16 can be used to make another point about molar volumes. Most solids are

more dense than the liquid of the same substance. Ice is one of the *few* exceptions, but it is so well known that students may be misled. You can make *tert*-butyl alcohol "cubes" (m.t. 21°C) or use Dry Ice and aluminum foil molds to freeze benzene. The demonstration and the results of Pr. 4-16 will convince the student. The structure of ice is unusual because of the hydrogen bonding arrangement. These matters will be discussed in Chapter 10, p. 185 and Chapter 17, p. 349 in the Textbook.

Demo. 15, LIQUID TO GAS CHANGE OF PHASE,

fits here. See p. 64 in the Laboratory Guide.

4-8 Review

You can perhaps add some reality to the gas properties in Table 4-5, Textbook p. 67, by having the student imagine he is a molecule in a gas. If a student were a 5-foot N_2 molecule (3.75 billion times larger than a real N_2 molecule) in air on an average day, then he would

- be traveling 1200 miles/hr on the average
- be 40 feet from his nearest neighbor
- travel 1100 ft between collisions
- collide with another "molecule" every 0.7 second

Note. In this example the distance scale has been enlarged but the time scale has not.

Supplementary Material

Films

For ordering information see the *List of Film Sources* at the back of the Teacher's Guide.

GAS PRESSURE AND MOLECULAR COLLISIONS

A CHEM Study film

Running Time: 21 minutes

The film explores the relationship between gas pressure and molecular collision through study of the effects of varying the number of molecules per unit volume and

of varying the temperature. The experimental study of the relative rates of effusion of H_2 , O_2 , CO_2 , and SF_6 leads to the quantitative relation between molar mass, molecular velocity, and absolute temperature. Mechanical models illustrate the experimental observations.

This film was produced in collaboration with Dr. J. A. Campbell. One part of it shows the relation of gas pressure to absolute temperature. In Section 4-2 we use the V - T relation. The film makes it clear that P - T could have been used and thus reinforces the connection between the gas regularities.

Background Discussion

The general intent of this chapter is to increase the student's confidence in scientific models by showing how helpful a good one is. For this reason the student should be made to understand how the kinetic theory explains gaseous behavior. This approach has several advantages:

1. It follows the flow of the course, emphasizing models and the scientific thought process.
2. It gives a method of working gas behavior problems based on understanding rather than on the mechanical solution of algebraic equations.
3. It introduces a number of concepts that are used here and later—absolute temperature, distribution of particle energy (the average energy is related to temperature), and partial pressure.

The following material includes these topics

Scientific Models

The Kinetic Energy Equation

The Gas Constant, R

Kinetic Energy and Absolute Temperature

Real Gases

Critical Conditions

These sections discuss some of the more complex aspects of gas behavior. You will not want to take these up in detail during your lectures. For some inquiring student, you can abstract what is needed for his questions.

Scientific Models

Our scientific probing represents a search for regularities. We seek to understand these regularities by constructing models of matter from which they might be predicted. Such a model, initially at least, is based on some familiar system whose behavior is clear. Frequently, however, the model must be so drastically modified that it bears little resemblance to familiar, well understood models. Often it reduces to a series of complex equations. But to remain useful the

model must accurately predict experimental behavior; this is the test which all models must pass.

Of the three phases of matter, the gaseous state is the best understood. The kinetic molecular theory was used to explain gas pressure in Chapter 2. Its application to the explanation of several other properties of gases is developed in this chapter. An excellent opportunity exists for developing the student's confidence in the power of a scientific model.

The Kinetic Energy Equation

In Chapter 4, the pressure exerted by a gas was explained in terms of the number of molecules n , their mass m , and their average velocity v . The proper "average velocity" is calculated by squaring each individual velocity, taking the average of these, and extracting the square root. This is called the root mean square velocity, and it is higher (8%) than a straight average. Just use the term "average velocity" without specifying. The number of collisions between a molecule and a given wall of a cubic container can be shown to be $v/2d$. For a large number of molecules, on the average only one-third of them would bombard a given wall, thus the total number of collisions with the one wall can be set equal to $nv/6d$. Each time a molecule strikes a wall and rebounds, it must reverse direction; hence the total change of momentum is $2mv$. Multiplying $2mv$ by the number of collisions per unit time yields this equation for the force exerted by the gas:

$$F = (nv/6d) \times 2mv = \frac{nmv^2}{3d} \quad (1)$$

Since pressure is force per unit area (d^2), equation (1) becomes

$$P = F/A = \frac{nmv^2}{3d^3} \quad (2)$$

Since d^3 defines a volume, equation (2) is commonly written

$$PV = \frac{1}{3}nmv^2 \tag{3}$$

which gives pressure times volume in terms of the mechanical properties of our model. The success of this equation is a rigorous test of the validity of our model.

If we consider one mole of gas, $n = N$. Then Nm (the number of molecules times the mass of one molecule) is M , the molar mass of the gas. Equation (3) can then be written (by setting $\frac{1}{3} = \frac{2}{3} \times \frac{1}{2}$)

$$PV = \frac{2}{3} \times \frac{1}{2}Mv^2 \tag{4}$$

The quantity $\frac{1}{2}Mv^2$ has been defined as kinetic energy (Sec. 4-4 of the Textbook), thus equation (4) can be written

$$\frac{2}{3} \times \frac{1}{2}Mv^2 = \frac{2}{3} \text{ K.E.} \tag{5}$$

But kinetic energy is related to absolute temperature.

$$\frac{1}{2}Mv^2 = cT$$

The constant c can be expressed as $\frac{3}{2}R$. The symbol R is called the gas constant. Substituting, we get, for one mole

$$PV = RT$$

or

$$\frac{PV}{T} = R \tag{6}$$

The Gas Constant, R

Equation (6) is often called the perfect gas law, and the constancy of this quotient provides another test of the validity of our kinetic molecular model. Some PV/T quotients for a mole of various gases have been computed and the results are recorded here in Table 4-1.

Although the values are not constant, they cluster close enough to an "ideal" value to suggest that our kinetic molecular model is a "good" model. Its predictions agree well with experimental values. The constant for an ideal gas (i.e., one defined by the kinetic molecular model) is 0.08206 liter-atm mole⁻¹ degree⁻¹. It can also be expressed in other units.

Observe that the experimental gas constant is

smaller than the ideal gas constant for all gases given except H₂ and He and that the constants for H₂, He, N₂, CO, and O₂ are close to the value for the ideal gas constant. The foregoing discussion has revealed some limitations of our model, but, as we shall see, those limitations do not destroy its utility. Rather, they have helped us to increase our understanding of real gases.

TABLE 4-1

Molar Gas Constant Values of Some Gases at 1 Atm and 0°C

R (liter-atm mole ⁻¹ degree ⁻¹)		R (liter-atm mole ⁻¹ degree ⁻¹)	
Gas		Gas	
H ₂	0.08213	CH ₄	0.08187
He	0.08211	CO ₂	0.08152
"Perfect" gas	0.08206	HCl	0.08146
N ₂	0.08203	NH ₃	0.08090
CO	0.08203	Cl ₂	0.08079
O ₂	0.08200	SO ₂	0.08015

Kinetic Energy and Absolute Temperature

As early as 1703 the effect of temperature on the pressure of a gas confined at constant volume was studied. For what we now call a one degree Celsius rise in temperature above 0°C the pressure of a gas increases $\frac{1}{273}$ of its pressure at 0°C. These findings can be summarized by the equation

$$P = P_0 + \frac{1}{273} P_0 t \tag{7}$$

where P is any pressure of the gas, P_0 is its pressure at 0°C, and t is temperature on the Celsius scale. Solving equation (7) for t yields

$$t = 273 \frac{P}{P_0} - 273 \tag{8}$$

If equation (8) can be assumed valid at all temperatures, it predicts that the pressure of the gas will become 0 at 273° below 0°C. In terms of our kinetic molecular model, this must mean that the motion of the particles has ceased completely—that they are absolutely frozen. This

state of complete rest is what the Textbook refers to as the absolute zero of temperature.

From this discussion, it appears that the temperature of a gas depends upon its molecular motion. The total kinetic energy of a gas has been defined as $\frac{1}{2}Mv^2$. Since mass cannot change with temperature, it must be v^2 which determines the temperature of a gas. For this reason we interpret the absolute temperature to be a measure of the square of the average velocity of the molecules of a gas.

Real Gases

Values of the gas constant for real gases listed in Table 4-1 indicate that certain gases such as CO_2 , HCl , NH_3 , Cl_2 , and SO_2 deviate considerably from ideal behavior. Although equation (6) predicts that the PV product will be a constant at a given temperature, it is found to vary with pressure, as shown in Figure 4-1.

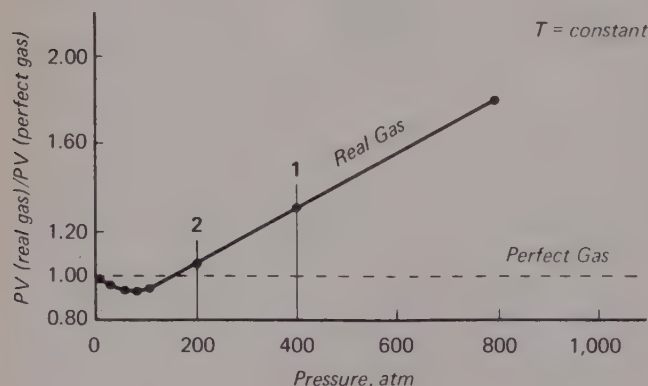


FIGURE 4-1

Variation of the PV product with pressure.

An examination of Figure 4-1 shows that when the gas expands from its volume at 400 atmospheres to its volume at 200 atmospheres, its PV product decreases (i.e., $P_1V_1 > P_2V_2$). We have shown by the previous discussion, and specifically by equation (4), that the PV product measures the kinetic energy or heat energy of a gas.

When a gas expands, its temperature usually changes. This effect was noticed in 1852 by J. P. Joule and W. Thomson, and is still called

the Joule-Thomson effect. The observed temperature change is the result of two factors: the separation of molecules against attracting forces; and the expansion of the gas, resulting from collisions and repulsive forces. Depending on the size of the two effects, this sum can be either a gain or loss of energy. Since the experiment is usually conducted under adiabatic conditions (no heat put in or taken out), the temperature can fall or rise.

Most gases, if not compressed too much or heated too much, will show a net cooling effect. Hydrogen and helium will warm at room temperature. Since curves such as those shown in Figure 4-1 vary with temperature, it is difficult to predict the conditions at which a gas will change from cooling to heating.

The decrease of energy that gases generally experience on expansion must be associated with some work done by the gas. Apparently it is the work necessary to overcome the attractive forces that are partly responsible for the deviation of the gas constant from the ideal value. They are called van der Waals forces, after one of the first investigators to explore them in great detail. As a result of his extensive research, van der Waals proposed an equation which reproduces the properties of real gases at relatively high pressures much better than the ideal gas equation (6). The van der Waals equation for one mole of gas is

$$(P + a/V^2)(V - b) = RT \quad (9)$$

Here a/V^2 is a correction factor for the attractive forces exerted by the molecules, and b is a correction factor for the volume actually occupied by the molecules. The corrective factors can be interpreted in the following manner. The actual force with which a molecule strikes the container wall (and thus the pressure we measure) is lower because the striking molecule is "held back" by the van der Waals attractive force. For this reason we add a correction to the observed pressure to approximate the ideal pressure. On the other hand, not all of the volume we measure for the gas sample (i.e., the volume of the container) is available to the molecules. Because they occupy some volume themselves, a correc-

tive factor proportional to that occupied volume must be subtracted to get closer to the true, available volume.

Critical Conditions

It is found experimentally (first by Andrews in 1869 for CO_2) that there is a temperature above

which a gas cannot be liquefied regardless of the applied pressure. This value is called the *critical temperature*, and the *critical pressure* is that which is just sufficient to produce liquid. Often these conditions are determined by watching the surface become fainter and disappear, since at the critical point liquid and gas are indistinguishable.

Answers to Exercises and Problems

Exercise 4-1

Start with 2 atmospheres pressure of oxygen and 1 atmosphere pressure of nitrogen in the experiment diagrammed in Figure 4-1. What would be the partial pressure of each gas after opening the stopcock? What would the final gas pressure be?

Answer

The two gases will each expand into the other volume as though it were empty. The new volume available to each gas is doubled so the new pressure will be half the original value.

$$p_{\text{O}_2} = 1 \text{ atm} \quad p_{\text{N}_2} = 0.5 \text{ atm}$$

Therefore

$$P_{\text{total}} = p_{\text{O}_2} + p_{\text{N}_2} = 1 + 0.5 = 1.5 \text{ atm}$$

Exercise 4-2

Suppose the flask containing O_2 is twice as large as the flask containing N_2 . If each gas initially is at one atmosphere pressure, what are the final partial pressures for each gas after the stopcock is opened? What is the final total pressure?

Answer

The volume for oxygen gas increases from 2 units to 3 units. The pressure of oxygen must decrease to $2/3$. The volume for nitrogen gas increases from 1 unit to 3 units. The pressure of nitrogen must decrease to $1/3$.

$$p_{\text{O}_2} = 2/3 \text{ atm}; \quad p_{\text{N}_2} = 1/3 \text{ atm}; \quad P_{\text{total}} = 1 \text{ atm}$$

Exercise 4-3

Express these temperatures in degrees Kelvin:

Water boils at	100°C
Mercury freezes at	-38.9°C
Nitrogen boils at	-196°C
Iron melts at	1535°C

Express these temperatures in degrees Celsius.

Lead melts at	600°C
Room temperature is	298°C
Helium boils at	4°C
Ammonia freezes at	195°C

Answer

Temperature of

boiling H_2O	373°C
freezing Hg	234°C
boiling N_2	77°C
melting Fe	1808°C
melting Pb	327°C
room	25°C
boiling He	-269°C
freezing NH_3	-78°C

Exercise 4-4

At a given temperature, the average KE_{trans} of the molecules in two different gases will be the same. Using NH_3 and HCl as the two gases, explain why NH_3 molecules will have higher velocities than HCl molecules, on the average.

Answer

$$KE = \frac{1}{2}mv^2$$

so we can write

$$(\frac{1}{2}mv^2)_{\text{NH}_3} = (\frac{1}{2}mv^2)_{\text{HCl}}$$

The masses of the individual molecules are equal to the molar mass divided by Avogadro's number. The molar masses are NH_3 17 g and HCl 36.5 g

$$\frac{1}{2}(17/6 \times 10^{23})v_{\text{NH}_3}^2 = \frac{1}{2}(36.5/6 \times 10^{23})v_{\text{HCl}}^2$$

$$v_{\text{NH}_3}^2 = (36.5/17)v_{\text{HCl}}^2$$

$$v_{\text{NH}_3} = \sqrt{36.5/17} v_{\text{HCl}}$$

The factor $\sqrt{36.5/17}$ is a bit over $\sqrt{2}$; its square root will be greater than 1. The velocity of NH_3 molecules is greater (by $\sqrt{36.5/17}$) than that of HCl molecules.

Exercise 4-5

Explain the experimental observation that diffusion occurs much more rapidly in a gas than in a solid or a liquid.

Answer

The gas molecules are much farther apart. Therefore they move farther between collisions and thus the progress of diffusion is more rapid. Note that, for equal temperatures, the gas particles are *not* moving more rapidly. They are just less impeded by other molecules.

Problem 1

What is the molar mass of a gas if 1.00 liter of the gas weighs 2.00 grams at 0°C and one atmosphere pressure?

Answer

At 0°C and one atm, one mole of gas occupies 22.4 liters.

Hence,

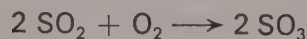
$$2.00 \frac{\text{g}}{\text{liters}} \times 22.4 \frac{\text{liters}}{\text{mole}} = 44.8 \frac{\text{g}}{\text{mole}}$$

Problem 2

The gas sulfur dioxide combines with oxygen to form the gas sulfur trioxide. What value would you expect for each of these ratios?

- $\frac{\text{number of SO}_3 \text{ molecules produced}}{\text{number of O}_2 \text{ molecules consumed}}$
- $\frac{\text{volume of SO}_3 \text{ gas produced}}{\text{volume of O}_2 \text{ gas consumed}}$

Answer



- Two. The balanced equation shows that two molecules of SO_3 are produced per molecule of oxygen consumed.
- Two. Since equal volumes contain equal numbers of molecules, two volumes of SO_3 will be produced for every volume of oxygen consumed.

Problem 3

Compressed oxygen gas is sold at a pressure of 130 atmospheres in steel cylinders of 40 liters volume.

- How many moles of oxygen are in one of these cylinders?
- How many kilograms of oxygen are in one of these cylinders?

Answer

A volume of 40 liters at 130 atmospheres would expand by a factor of 130/1 if the pressure were reduced to one atmosphere. Therefore the cylinder contains enough oxygen to occupy

$$130/1 \times 40 = 5.2 \times 10^3 \text{ liters}$$

at one atmosphere.

- Since one mole occupies 24.5 liters at room temperature and one atmosphere, the cylinder contains

$$\frac{5.2 \times 10^3 \text{ liters}}{24.5 \text{ liters/mole}} = 2.1 \times 10^2 \text{ moles}$$

- Mass of oxygen = $(2.1 \times 10^2 \text{ moles}) \times (32.0 \text{ g/mole}) = 6.7 \times 10^3 \text{ g}$ or 7 kg

Problem 4

A 1.50 liter sample of dry air in a cylinder exerts a pressure of 3.00 atmospheres at a temperature of 25°C . Without change in temperature, a piston is moved in the cylinder until the pressure in the cylinder is reduced to 1.00 atmosphere. What is the volume of the gas?

Answer

The amount of gas is constant, and the temperature is constant; hence the behavior is consistent with the regularity

$$PV = \text{constant}$$

Decreasing the pressure by a factor of three (3.00 atm/1.00 atm) increases the volume by the same factor.

$$\text{Final volume} = \left(\frac{3.00}{1.00} \right) \times 1.50 \text{ liters} = 4.50 \text{ liters}$$

Problem 5

Suppose the total pressure in an automobile tire is 30 pounds/inch² and we want to increase the pressure to 40 pounds/inch². What change in the amount of air in the tire must take place? Assume that the temperature and volume of the tire remain constant.

Answer

The pressure is increased by the factor 40/30. Since volume and temperature are constant, the number of moles of gas in the tire must be increased by the same factor.

Problem 6

A student collects a volume of hydrogen over water. He determines that there are 2.00×10^{-3} mole of hydrogen and 6.0×10^{-5} mole of water vapor present. If the total pressure inside the collecting tube is 760 mm, what is the partial pressure of each gas?

Answer

$$\begin{aligned}\text{Moles H}_2 &= 0.00200 \\ \text{Moles H}_2\text{O} &= 0.000060 \\ \text{Total moles} &= 0.00206\end{aligned}$$

$$\text{Partial pressure} = \frac{\text{fraction of total moles}}{\text{total pressure}}$$

$$\begin{aligned}\text{Partial pressure of H}_2 &= \frac{0.00200}{0.00206} \times 760 \text{ mm} \\ &= 738 \text{ mm}\end{aligned}$$

$$\begin{aligned}\text{Partial pressure of H}_2\text{O} &= \frac{0.000060}{0.00206} \times 760 \text{ mm} \\ &= 22 \text{ mm}\end{aligned}$$

Problem 7

A sample of nitrogen is collected over water at 18.5°C. The vapor pressure of water at 18.5°C is 16 mm. What are the partial pressures of nitrogen and of water if the total pressure is 756 mm?

Answer

The partial pressure of water is the vapor pressure, 16 mm. The remainder of the pressure ($756 - 16 = 740$ mm) is the partial pressure of nitrogen.

Problem 8

A cylinder contains nitrogen gas and a small amount of liquid water at a temperature of 25°C (the vapor pressure of water at 25°C is 23.8 mm). The total pressure is 600.0 mm. A piston is pushed into the cylinder until the volume is halved. What is the final total pressure?

Answer: 1176 mm.

Answer

Initially the total pressure is 600.0 mm. The partial

pressure of water is 23.8 mm. Hence the partial pressure of nitrogen is

$$600.0 - 23.8 = 576.2 \text{ mm}$$

When the volume is halved, the nitrogen partial pressure is doubled ($PV = \text{a constant}$) to give 1152.4 mm. The partial pressure of water, however, remains equal to the vapor pressure, 23.8 mm. Hence the observed pressure is

$$1152.4 + 23.8 = 1176.2 \text{ mm.}$$

Problem 9

Why does the pressure build up in a tire on a hot day? Answer in terms of the Kinetic Theory.

Answer

As the temperature of the air molecules rises, the kinetic energy increases. Since the volume of a tire remains almost constant, the increased velocity of the air molecules results in more collisions per unit time with the tire walls, and the force exerted per collision is greater. Thus the pressure rises.

Problem 10

Two glass containers have the same volume. One is filled with hydrogen gas, the other with carbon dioxide gas. Both containers are at the same temperature and pressure.

- Compare the number of moles of the two gases.
- Compare the number of molecules of the two gases.
- Compare the number of grams of the two gases.
- The temperature of the container of hydrogen gas is increased. Now compare the pressure, the volume, the number of moles, and the average molecular kinetic energy.

Answer

- Equal (by Avogadro's Hypothesis).
- Equal (by Avogadro's Hypothesis).
- The masses are in the ratio of the molar mass. CO_2 is heavier by the factor $44.0/2.02 = 21.8$.
- The bulb has higher pressure.
 - The volumes remain the same.
 - The number of moles remains equal because the bulbs are closed.
 - The average kinetic energy of the hydrogen molecules will be higher because the temperature is higher.

Problem 11

Why is it desirable to express all temperatures in degrees Kelvin when working problems dealing with gas relationships?

Answer

Either °C or °K can be used in determining volume (or pressure) changes caused by changing temperature. However, using the Kelvin scale is much simpler, for volume varies directly with it.

Problem 12

The boiling and freezing temperatures of certain liquids are listed below. Express these temperatures on the absolute temperature scale.

Liquid helium	boiling temperature	-269°C
Liquid hydrogen	freezing temperature	-259°C
Liquid hydrogen	boiling temperature	-253°C
Liquid nitrogen	freezing temperature	-210°C
Liquid nitrogen	boiling temperature	-196°C
Liquid oxygen	freezing temperature	-219°C
Liquid oxygen	boiling temperature	-183°C

Answer

Liquid helium	b.t. = 4°K
Liquid hydrogen	f.t. = 14°K
Liquid hydrogen	b.t. = 20°K
Liquid nitrogen	f.t. = 63°K
Liquid nitrogen	b.t. = 77°K
Liquid oxygen	f.t. = 54°K
Liquid oxygen	b.t. = 90°K

Problem 13

How many molecules are there in a molar volume of a gas at 100°C? at 0°C?

Answer

There are 6.0×10^{23} molecules (Avogadro's number). A "molar volume" means "the volume occupied by one mole." Hence, a molar volume at any conditions contains 6.0×10^{23} molecules.

Problem 14

If 1.00×10^2 ml of a gas at 10°C are heated to 20°C, the volume of the gas will be approximately: (Pressure and number of molecules are kept constant.)

- (a) 50 ml
- (b) 100 ml
- (c) 103 ml
- (d) 200 ml
- (e) 375 ml

Answer

- (c) Approximately 103 ml. Change °C to °K by adding 273°; then since the temperature is increasing, the volume will increase to 293/283 of the original:

$$100 \text{ ml} \times \frac{293}{283} = 103 \text{ ml}$$

Problem 15

What is the molar volume of water under each of the following conditions?

- (a) Solid, 0°C. Density of ice = 0.915 g/ml
- (b) Liquid, 0°C. Density of water = 1.00 g/ml
- (c) Gas, 100°C. Density of water vapor (100°C and 1 atm) = 5.88×10^{-4} g/ml

Answer

- (a) Molar volume of ice, 0°C;

$$\frac{18.0 \text{ g/mole}}{0.915 \text{ g/ml}} = 19.7 \text{ ml/mole}$$

- (b) Molar volume of liquid water, 0°C;

$$\frac{18.0 \text{ g/mole}}{1.00 \text{ g/ml}} = 18.0 \text{ ml/mole}$$

- (c) Molar volume of water vapor, 100°C;

$$\frac{18.0 \text{ g/mole}}{5.88 \times 10^{-4} \text{ g/ml}} = 3.06 \times 10^4 \text{ ml/mole}$$

Problem 16

Compare your answers in Problem 15 with the values for ammonia given on page 65. You know that an ice cube floats in water. Would an ammonia "ice cube" float or sink in liquid ammonia?

Answer

Table 4-4 shows that solid NH_3 weighs 0.81 g/cm³. The piece of solid ammonia would *sink* in liquid NH_3 (0.68 g/cm³).

Problem 17

A carbon dioxide fire extinguisher of 3 liters volume contains 4.4 kilograms of CO_2 . What volume of gas could this extinguisher deliver at 25°C and one atm pressure?

Answer

$$4.4 \text{ kg} = 4.4 \times 10^3 \text{ g} = \frac{4.4 \times 10^3 \text{ g}}{44 \text{ g/mole}} = 1.0 \times 10^2 \text{ moles}$$

One mole occupies 24.5 liters at room conditions. Hence 1.0×10^2 moles occupy $(1.0 \times 10^2) \times (24.5)$ liters or about 2500 liters.

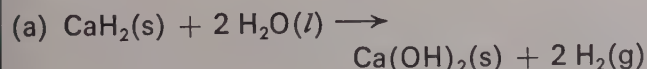
(Notice that the 3 liter volume does not enter the calculation. It does, however, show that the extinguisher contains a condensed phase, liquid CO_2 , giving the 1000-fold volume change on vaporization.)

Problem 18

Hydrogen for weather balloons is often supplied by the reaction between solid calcium hydride, CaH_2 , and water to form solid calcium hydroxide, Ca(OH)_2 , and hydrogen gas.

- Balance the equation for the reaction between water and calcium hydride.
- How many moles of CaH_2 would be required to fill a weather balloon with 250 liters of hydrogen at 25°C and one atm pressure?
- What mass of water would be required to generate the hydrogen?

Answer



- $\frac{250 \text{ liters}}{24.5 \text{ liters/mole}}$ or about 10 moles H_2 gas

are needed.

By the balanced equation, it takes 5.0 moles of CaH_2 to produce 10 moles of H_2 .

- By the equation, it takes ten moles of water to produce ten moles of H_2 .
Ten moles of H_2O weigh

$$(10 \text{ moles}) \times \left(\frac{18 \text{ g}}{\text{mole}} \right) = 180 \text{ g, or } 0.18 \text{ kg}$$

Problem 19

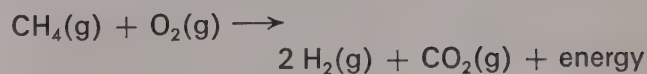
A gas phase reaction between methane, CH_4 , and oxygen, O_2 , is carried out in a sealed container. Under the conditions used, the products are carbon dioxide and hydrogen. The reaction is exothermic so the temperature rises during the reaction.

- Will the final pressure be greater or less than the original pressure?
- By what factor does the pressure change if one mole of methane and one mole of oxygen react (the temperature changes from 25°C to 200°C)?

Answer: 2.38.

Answer

The balanced equation is



- Two moles of reactants give three moles of products, resulting in a pressure rise. The temperature rise also causes a pressure rise. Since the effects reinforce, the final pressure must be greater than the initial pressure.
- The pressure increases by a factor of 1.5 due to the change in the number of moles. There is an additional pressure change due to the increase in temperature, which rises by a factor $473/298 = 1.59$.

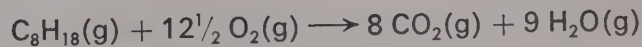
The pressure rises by the factor
 $(1.50) \times (1.59) = 2.38$.

Problem 20

Combustion of gasoline, typical formula C_8H_{18} , provides the energy to propel an automobile. As the gasoline burns in the car cylinder, the pressure increases and forces the piston down. This motion in turn is transmitted to the wheels of the car. Oxygen reacts with the gasoline to form carbon dioxide and water, releasing enough energy to heat the gas from 300°K to about 1500°K .

- Balance the equation for the reaction.
- Decide whether the work done by the gas in the cylinder is mainly the result of pressure rise caused by the change in number of moles of gas or the result of pressure rise from heating.

Answer



Thus $13\frac{1}{2}$ moles of reactants give 17 moles of products, increasing the pressure by a factor of

$$17.0/13.5 = 1.26$$

The temperature rise causes pressure to change by the factor

$$1500/300 = 5$$

Most of the pressure rise is caused by the increased temperature.

Problem 21

A vessel contains equal numbers of oxygen and hydrogen molecules. The pressure is 760 mm when the volume is 50 liters. Which of these statements is FALSE?

- On the average, the hydrogen molecules are traveling faster than the oxygen molecules.
- On the average, more hydrogen molecules strike the walls per second than oxygen molecules.
- If the oxygen were removed from the system, the pressure would drop to 190 mm.
- Equal numbers of moles of each gas are present.
- The average kinetic energies of oxygen and hydrogen molecules are the same.

Answer

Part (c) is false. The pressure would drop to 380 mm Hg.

Problem 22

The vapor pressure of a molten metal can be measured with a device called a Knudsen cell. This is a container closed across the top by a thin foil pierced by a small hole of known diameter. The cell is heated in a vacuum until the vapor streams from the small hole (it *effuses*). The mass of the material escaping per second tells the rate at which gaseous atoms leave. Two identical Knudsen cells are heated at 1000°C. One cell contains lead and the other cell contains magnesium.

- Contrast the average kinetic energies of the lead and magnesium atoms within each cell.
- Contrast the average velocities of the lead and magnesium atoms leaving each cell.
- At a fixed temperature, the rate at which atoms leave the cell is determined by two factors, the vapor pressure and the mass of the gaseous atoms. Explain.

Answer

- Since the two gases are at the same temperature, they have the same average kinetic energy.
- Since the two gases have the same kinetic energy, the magnesium atoms, having much lower mass, must have much higher velocities.
- The number of atoms leaving per second is determined by the number of "collisions" per second of gaseous atoms with the hole. The vapor pressure indicates the number of molecules per unit volume, and the higher the vapor pressure, the more molecules that strike the surface per second. In addition, the higher the molecular mass, the slower the particles are moving at a given temperature. Hence both vapor pressure and molecular

mass are important in fixing the number of atoms leaving the cell per second.

(Note: The vapor pressure of lead at 1000°C is about 1.2 mm, and that of magnesium at 1000°C is about 210 mm.)

Problem 23

The boiling temperatures and the molar volumes at STP of some common gases are listed in the following table.

- What regularity is suggested in the relationship between the boiling temperatures and molar volumes?
- Account for this regularity.

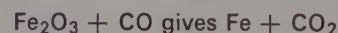
Gas	Molecular Formula	Boiling Temperature (°C)	Molar Volume (liters)
helium	He	-269	22.426
nitrogen	N ₂	-196	22.402
carbon monoxide	CO	-190	22.402
oxygen	O ₂	-183	22.393
methane	CH ₄	-161	22.360
hydrogen chloride	HCl	-84.0	22.248
ammonia	NH ₃	-33.3	22.094
chlorine	Cl ₂	-34.6	22.063
sulfur dioxide	SO ₂	-10.0	21.888

Answer

- The lower-boiling-temperature substances show less deviation from "ideality." Their molar volumes are more nearly equal to the 22.414 liter molar volume predicted for ideal gases at STP. The departure from ideality increases for gases having boiling temperatures closer to the specified temperature, 0°C.
- For those with higher boiling temperatures, the attractions between the molecules are greater, and hence they depart more from ideality. If these gases were heated (or if the pressure were reduced), the molecules could move farther apart, and the molar volume would approach 22.414 liters.

Problem 24

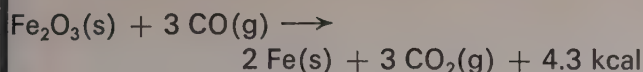
A reaction involved in the production of iron from iron ore is



- How many kilograms of CO are needed to produce 1.0 kg of Fe?
- How many liters of CO (at STP) are needed to produce 1.0 kg of Fe?

Answer

The balanced equation is



$$\begin{aligned} \text{(a) moles Fe} &= (1.0 \times 10^3 \text{ g Fe}) \left(\frac{1 \text{ mole Fe}}{56 \text{ g Fe}} \right) \\ &= 18 \text{ moles Fe} \end{aligned}$$

$$\begin{aligned} &\left(\frac{3 \text{ moles CO}}{2 \text{ moles Fe}} \right) (18 \text{ moles Fe}) \left(\frac{28 \text{ g CO}}{\text{mole CO}} \right) \\ &\times \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = \left(\frac{3}{2} \right) (18) (28) \left(\frac{1}{1000} \right) = 0.75 \text{ kg} \\ &= 0.8 \text{ kg CO required.} \end{aligned}$$

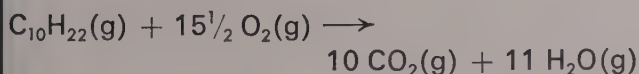
$$\begin{aligned} \text{(b) moles CO} &= (\text{moles Fe}) \left(\frac{\text{moles CO}}{\text{mole Fe}} \right) \\ &= 18 \times \frac{3}{2} = 27 \text{ moles} \end{aligned}$$

$$\begin{aligned} \text{vol CO (STP)} &= (\text{moles CO}) (\text{liters/mole}) \\ &= 27 \times 22.4 \\ &= 6.0 \times 10^2 \text{ liters} \end{aligned}$$

Problem 25

A compound found in kerosene, a mixture of hydrocarbons, is decane, $\text{C}_{10}\text{H}_{22}$. A stove might burn 1.0 kg of kerosene per hour. Assume kerosene is decane.

- (a) How many liters of oxygen at STP are needed per hour?
 (b) How many liters of carbon dioxide at STP are produced per hour?

Answer

$$\begin{aligned} \text{(a) g C}_{10}\text{H}_{22} / \text{molar mass C}_{10}\text{H}_{22} &= \text{moles C}_{10}\text{H}_{22} \\ (1.0 \times 10^3) / 142 &= 7.0 \text{ moles C}_{10}\text{H}_{22} \end{aligned}$$

$$(\text{moles C}_{10}\text{H}_{22}) \left(\frac{\text{moles O}_2}{\text{mole C}_{10}\text{H}_{22}} \right) = \text{moles O}_2$$

$$7.0 \times \frac{15.5}{1} = 108 \text{ moles O}_2$$

Amount of oxygen needed to burn 1.0 kg $\text{C}_{10}\text{H}_{22}$:

$$(\text{moles O}_2) \left[\frac{\text{liters (STP)}}{\text{mole}} \right]$$

$$108 \times 22.4 = 2420 \text{ liters} = 2.4 \times 10^3 \text{ liters}$$

$$\text{(b) } (\text{moles C}_{10}\text{H}_{22}) \left(\frac{\text{moles CO}_2}{\text{mole C}_{10}\text{H}_{22}} \right) = \text{moles CO}_2$$

$$7.0 \times \frac{10}{1} = 70 \text{ moles CO}_2$$

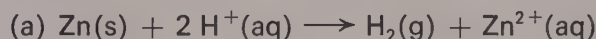
Amount of CO_2 produced from 1.0 kg $\text{C}_{10}\text{H}_{22}$:

$$(\text{moles CO}_2) \left[\frac{\text{liters (STP)}}{\text{mole CO}_2} \right]$$

$$70 \times \frac{22.4}{1} = 1570 \text{ liters} = 1.6 \times 10^3 \text{ liters}$$

Problem 26

How many grams of zinc metal are needed to react with hydrochloric acid to produce enough hydrogen gas to fill an 11.2 liter balloon at STP? What would the volume of this balloon be at 27°C and 680 mm pressure? How many grams of zinc would be required if sulfuric acid were used instead of hydrochloric acid?

Answer

$$\begin{aligned} \text{moles H}_2 &= [\text{vol H}_2 \text{ (STP)}] / [\text{liters per mole (STP)}] \\ &= 11.2 / 22.4 = 0.500 \text{ mole H}_2 \end{aligned}$$

$$(\text{moles H}_2) \left(\frac{\text{moles Zn}}{\text{mole H}_2} \right) = \text{moles Zn}$$

$$0.500 \times \frac{1}{1} = 0.500 \text{ mole Zn}$$

$$\begin{aligned} (\text{moles Zn}) (\text{molar mass Zn}) &= \text{grams Zn} \\ 0.500 \times 65.4 &= 32.7 \text{ g Zn} \end{aligned}$$

$$\text{(b) } (11.2 \text{ liters}) \left(\frac{27^\circ\text{K} + 273^\circ\text{K}}{273^\circ\text{K}} \right) \left(\frac{760 \text{ mm}}{680 \text{ mm}} \right)$$

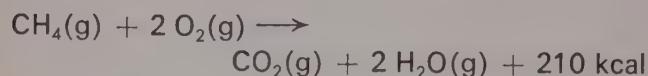
$$= 13.8 \text{ liters at new conditions}$$

- (c) Same as (a). One mole of Zn gives one mole of H_2 , regardless of the source of the H^+ reacting.

Problem 27

How many liters of air at STP are needed to burn 2.2 liters of methane, also at STP? Assume air is 20% oxygen by volume.

Answer



$$\begin{aligned} \text{moles CH}_4 &= (\text{vol CH}_4) / (\text{liters per mole}) \\ 2.2 / 22.4 &= 0.098 \text{ mole CH}_4 \end{aligned}$$

$$(\text{moles CH}_4) \left(\frac{\text{moles O}_2}{\text{mole CH}_4} \right) = \text{moles O}_2$$

$$0.098 \times \frac{2}{1} = 0.196 \text{ mole}$$

or

$$0.20 \text{ mole O}_2$$

$$(\text{moles O}_2) \left(\frac{\text{moles air}}{\text{mole O}_2} \right) = \text{moles air}$$

$$0.20 \times \frac{5}{1} = 1.0 \text{ mole air}$$

$$(\text{moles air}) \left[\frac{\text{liters (STP)}}{\text{mole}} \right]$$

$$1.0 \times 22.4 = 22.4 \text{ liters}$$

or

$$22 \text{ liters}$$

Or simply evoke Avogadro's Hypothesis and note from the equation that one liter of CH₄ requires 2 liters of O₂. In this problem the 4.4 liters of O₂ needed would be contained in 5 × 4.4 = 22 liters of air.

Problem 28

In the reaction NH₃ + O₂ gives NO + H₂O, how many liters of oxygen are required to react with 4.48 liters of ammonia? All gases are measured at STP.

Answer



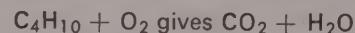
When reacting gases are at the same temperature and pressure, the volume ratio is equal to the mole ratio (Avogadro's Hypothesis).

$$\left(\frac{\text{volume O}_2}{\text{needed}} \right) = \left(\frac{\text{volume NH}_3}{\text{consumed}} \right) \left(\frac{\text{moles O}_2}{\text{mole NH}_3} \right)$$

$$\text{vol O}_2 = 4.48 \text{ liters} \times \frac{2.5}{2} = 5.60 \text{ liters}$$

Problem 29

The following reaction is carried out with all gas volumes measured at the same temperature and pressure.



- How many liters of oxygen are required to produce 2.0 liters of CO₂?
- If 15 liters of oxygen are used, how many liters of butane, C₄H₁₀, will be burned?
- If 8.0 liters each of oxygen and butane are mixed, how many liters of CO₂ are produced?

Answer



When reacting gases are at the same temperature and pressure, the volume ratio is equal to the mole ratio (Avogadro's Hypothesis).

$$(a) \left(\frac{\text{volume O}_2}{\text{consumed}} \right) = \left(\frac{\text{volume CO}_2}{\text{produced}} \right) \left(\frac{\text{moles O}_2}{\text{mole CO}_2} \right)$$

$$\text{vol O}_2 = 2.0 \text{ liters} \times \frac{6.5}{4.0} = 3.2 \text{ liters}$$

$$(b) \left(\frac{\text{volume C}_4\text{H}_{10}}{\text{burned}} \right) = \left(\frac{\text{volume O}_2}{\text{consumed}} \right) \left(\frac{\text{moles C}_4\text{H}_{10}}{\text{mole O}_2} \right)$$

$$\text{vol C}_4\text{H}_{10} = 15 \text{ liters} \times \frac{1}{6.5} = 2.3 \text{ liters}$$

- Since equal numbers of moles of C₄H₁₀ and O₂ are present initially, and since one mole of C₄H₁₀ reacts with 6.5 moles of O₂, the C₄H₁₀ is present in excess. The reaction will proceed until the oxygen is consumed.

$$\left(\frac{\text{volume CO}_2}{\text{produced}} \right) = \left(\frac{\text{volume O}_2}{\text{consumed}} \right) \left(\frac{\text{moles CO}_2}{\text{mole O}_2} \right)$$

$$\text{vol CO}_2 = 8.0 \text{ liters} \times \frac{4}{6.5} = 4.9 \text{ liters}$$

Problem 30

What volume of Cl_2 gas at 37°C and 753 mm pressure could be obtained from 58.4 liters of HCl , measured at the same temperature and pressure, if the following reaction takes place?

**Answer**

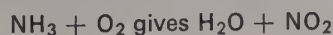
When reacting gases are at the same temperature and pressure, the volume ratio is equal to the mole ratio (Avogadro's Hypothesis).

$$\left(\frac{\text{volume Cl}_2}{\text{produced}} \right) = \left(\frac{\text{volume HCl}}{\text{consumed}} \right) \left(\frac{\text{moles Cl}_2}{\text{mole HCl}} \right)$$

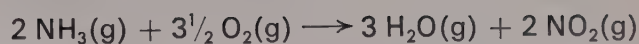
$$\text{vol Cl}_2 = 58.4 \text{ liters} \times \frac{2}{4} = 29.2 \text{ liters}$$

Problem 31

Suppose 105 liters of NH_3 and 285 liters of O_2 are allowed to react until this reaction is complete.



All volume measurements are made at 200°C and 0.30 atm pressure. Which gas, ammonia or oxygen, remains at the end of the reaction? How many moles of it would there be?

Answer

Since conditions are maintained at 200°C and 0.30 atmosphere, the mole ratio will equal the volume ratio (Avogadro's Hypothesis).

Amount of O_2 needed to use 105 liters of NH_3 :

$$(\text{liters NH}_3) \left(\frac{\text{liters O}_2}{\text{liter NH}_3} \right)$$

$$105 \times \frac{3.5}{2} = 184 \text{ liters}$$

This volume of O_2 is available, and, indeed, an excess of $285 - 184 = 101$ liters of oxygen will be unreacted.

$$(101 \text{ liters}) \times \left(\frac{1 \text{ mole}}{\left(22.4 \times \frac{1}{0.3} \times \frac{473}{273} \right) \text{ liters}} \right)$$

$$= 0.78 \text{ mole}$$

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

In an experiment similar to Experiment 5, an empty (evacuated) container was weighed, then filled with oxygen, and weighed again. The container was again evacuated and weighed when filled with an unknown gas. Both gases were weighed at the same temperature and pressure. Use following data for Questions 1–3.

Container empty	150.10 g
Container + oxygen gas	151.41 g
Container + unknown gas	151.82 g

- Using Avogadro's Hypothesis calculate the molar mass of the unknown gas. Show your calculations.

Answer

Molar mass

$$= \frac{\text{mass unknown gas}}{\text{mass equal vol O}_2} \times 32.0 \text{ g/mole}$$

Molar mass

$$= \frac{1.72 \text{ g}}{1.31 \text{ g}} \times 32.0 \text{ g/mole} = 42.0 \text{ g/mole}$$

- It is determined experimentally that the unknown gas contains carbon and hydrogen atoms in the ratio of 1/2. What is the simplest formula?

Answer: CH_2 .

3. Using the molar mass obtained in question 1, and the simplest formula from question 2, determine the correct molecular formula for the unknown gas.

Answer: C_3H_6 .

4. A flask of nitrogen is collected over water at a total pressure of 740 mm of mercury. If the partial pressure of the water vapor is 15 mm of mercury, what is the pressure exerted by the nitrogen?

Answer

$$p_{N_2} + p_{H_2O} = P_{\text{total}}$$

$$p_{N_2} = 740 \text{ mm} - 15 \text{ mm} = 725 \text{ mm Hg}$$

5. A particular gas sample is 1% oxygen molecules. How many oxygen molecules are there in one liter of the gas sample at STP?

Answer

$$\begin{aligned} (6.0 \times 10^{23}) \times \left(\frac{1}{22.4}\right) \left(\frac{1}{100}\right) \\ = 2.68 \times 10^{20} \text{ O}_2 \text{ molecules/liter} \end{aligned}$$

Questions 6–9 refer to the following data.

A flask is filled with a mixture of two gases, oxygen (O_2) and sulfur dioxide (SO_2). Initially, the pressure in the container is 1500 mm, and the temperature is 20°C . One gram of each gas is present. No chemical reaction occurs between the two gases under these conditions.

6. What is the partial pressure exerted by each of the gases?

Answer

$$\frac{1 \text{ g}}{32 \text{ g/mole}} = \frac{1}{32} \text{ mole oxygen}$$

$$\frac{1 \text{ g}}{64 \text{ g/mole}} = \frac{1}{64} \text{ mole sulfur dioxide}$$

Since there are twice as many moles of oxygen as there are of sulfur dioxide, the partial pressure of oxygen, p_{O_2} , is twice the partial pressure of sulfur dioxide, p_{SO_2} .

$$\begin{aligned} p_{SO_2} + p_{O_2} &= 1500 \\ p_{O_2} &= 2p_{SO_2} \\ p_{SO_2} + 2p_{SO_2} &= 1500 \\ p_{SO_2} &= 500 \text{ mm} \end{aligned}$$

and

$$p_{O_2} = 1000 \text{ mm}$$

7. If atmospheric pressure is 750 mm, and if the flask is opened to equalize the pressure inside and outside the container and then closed again, how many moles of each gas will remain in the container? (Assume that the temperature remains constant at 20°C .)

Answer

$$\frac{1}{32} \text{ mole} \times \frac{750 \text{ mm}}{1500 \text{ mm}} = \frac{1}{64} \text{ mole}$$

$$\frac{1}{64} \text{ mole} \times \frac{750 \text{ mm}}{1500 \text{ mm}} = \frac{1}{128} \text{ mole}$$

8. What temperature would be needed to increase the gas pressure to its original value of 1500 mm?

Answer

To double the pressure the absolute temperature must be doubled, the volume and amount remaining constant.

$$20^\circ\text{C} = 293^\circ\text{K}$$

$$2 \times 293^\circ\text{K} = 586^\circ\text{K} = 313^\circ\text{C}$$

9. How does the average kinetic energy of the oxygen molecules compare to the average kinetic energy of the sulfur dioxide molecules at 20°C ?

Answer: They are the same.

10. The molar volume of a gas varies with pressure and is quite low at high pressure. The density of CO_2 gas at 210°C and 30 atm is 0.0334 g/ml.

(a) What is the molar volume at these conditions?

(b) How many molecules does this volume contain?

Answer

$$(a) \frac{44}{0.0334} = 1320 \text{ ml/mole}$$

or 1.32 liters/mole

$$(b) 6.0 \times 10^{23}$$

Questions 11–13 refer to the following description.

Consider the following system as a scientific model describing a container filled with a gas. Some small spheres are added to an evacuated cylinder closed by a movable piston. Imagine the spheres to be in continuous random motion. They are also perfectly elastic—they rebound after colliding with each other or with the walls of the container without losing energy.

11. In order for our model to be analogous to a gaseous system, what must happen to the spheres in our model if the temperature is increased?

Answer: They move faster.

12. What would happen to the piston if the temperature were increased?

Answer: The piston would move up.

13. What would happen to the pressure if the piston were fixed in place and the temperature raised?

Answer: The pressure would rise.

14. A welder has a cylinder of helium used in arc welding. The cylinder volume is 32 liters and the gas pressure is 110 atm at 25°C. The cylinder will burst if the pressure reaches 200 atmospheres. Which of the following is FALSE?

- (1) The cylinder contains 144 moles of He.
- (2) The He could fill a 3500 liter balloon at 25°C.
- (3) The welder can safely heat the cylinder to 325°C.
- (4) The pressure in mm Hg is 8.4×10^4 .
- (5) Half again as much helium could be safely added to the cylinder.

Answer

Statement (3) is false. $325^\circ\text{C} \cong 600^\circ\text{K}$. At this temperature the pressure would be 220 atmospheres.

Questions 15 and 16 need the following fact.

A fire extinguisher contains 4.4 kg of liquid CO_2 .

15. How many liters of gas will be released when the extinguisher is emptied? Assume STP.

Answer

$$\left(\frac{4400 \text{ g CO}_2}{44 \text{ g CO}_2/\text{mole}} \right) \left(\frac{22.4 \text{ liters (STP)}}{\text{mole}} \right) = 2240 \text{ liters or } 2200 \text{ liters}$$

This volume is large enough to warrant ignoring the few liters remaining in the extinguisher.

16. How many grams of carbon are needed to produce the CO_2 in the extinguisher?

Answer

$$\left(\frac{4400 \text{ g CO}_2}{44 \text{ g CO}_2/\text{mole}} \right) \left(\frac{1 \text{ mole C}}{\text{mole CO}_2} \right) \left(\frac{12 \text{ g C}}{\text{mole}} \right) = 1200 \text{ g C needed}$$

Liquids and Solids

An Extension of the Kinetic Theory



Intent and Approach

Chapter 5 is a logical extension of Chapter 4, but applies the kinetic theory to molecular motions and interactions in solids and liquids.

Keep in mind that Chapter 5 is intended only as a brief introduction to the structure of solids and liquids. For this reason, several topics first mentioned here are developed in more detail later. For example, Chapter 17 considers the properties of some solids and liquids in terms of the more detailed concepts of the chemical bond.

On the other hand, the topic of phase equilibrium is not treated elsewhere. Explanations needed for this topic arise from the kinetic theory,

and can be developed fairly well now. The background section extends the Textbook discussion of liquids, solutions, and phase equilibria. You will not have time to present any appreciable amount of this detail to the student, but you may find review of this material helpful. Potential energy is also an important topic in this chapter.

We also find that it is convenient to introduce and use a number of new terms. Remember, however, that you should emphasize the *new concepts*, not the new terms. New words are used to simplify our presentation; don't lose the student in a maze of terminology.

Outline

Potential energy, and especially its conversion to kinetic energy, is taken up first (5-1).

Next, solid-liquid phase changes are discussed (5-2) and then liquid-gas phase changes (5-3). Melting and boiling temperatures and the molar heats of these changes are introduced.

Vapor pressure furnishes the first example of dynamic equilibrium (5-4). The variation of vapor pressure with temperature gives a rational basis for understanding boiling (5-5).

The solid-gas phase change is mentioned (5-6). A review is included (5-7).

New Concepts

1. Potential-kinetic energy related to particle movement, particularly in collisions.
2. Solid-liquid phase change; melting; molar heat of melting.
3. The liquid-vapor equilibrium in molecular terms; molar heat of vaporization.
4. The vapor pressure of liquids, the factors affecting it, and the relation between vapor pressure and boiling temperature.
5. Solid-vapor equilibrium

SCHEDULE AND RELATED MATERIAL

Suggested Time : 8 days

Text Section	Topic and Other Work	Exercises	Problems		
			Easy	Medium	Hard
5-1	Potential Energy Expt. 12. Warming and Cooling Behavior Expt. 13. Energy Needed to Melt Ice Expt. 14. Energy of Crystallization		1, 4	2	3
5-2	Solid-Liquid Phase Change		5, 6	7, 8	9, 10
5-3	Liquid-Gas Phase Change Demo. 16. Vapor and Liquid Temperatures during Boiling	1	11, 13, 17	12, 14, 16, 18, 19	15, 20, 21
5-4	Vapor Pressure in Liquid-Vapor Equilibrium Demo. 17. Vapor Pressure at Two Temperatures	2		22, 23	
5-5	Change of Vapor Pressure with Temperature	3	25-27	24, 28, 29	
5-6	Vapor Pressure in Solid-Vapor Equilibrium Demo. 18. Vapor Pressure of I ₂		30		
5-7	Review				

Development

5-1 Potential Energy

In this section we consider an ideal case. The carts are considered to roll without friction and the spring to be perfectly elastic. Actual conditions fall short of such perfection in varying degrees, and some of the work produces heat. A similar situation would hold if we looked at the collision of inelastic spheres. Try rolling two putty balls together. You will see that kinetic energy is not conserved. Some of it goes into deforming (and heating) the balls.

Do not get into a discussion of the nonideal features of our model. If some question about friction arises, admit it exists, but stress our interest in the ideal case. Remind the student

that, since we will be concerned with the motion of atoms or molecules moving in space, the topic of friction is of less importance to us than to a physicist or mechanical engineer. Particles of a gas, in particular, have essentially no interaction in many cases.

The student is going to meet the concepts of potential energy and its interchange to kinetic energy in many places during the course. He will learn of "storing" energy by forming new atomic arrangements in Chapters 10 and 11; by new electronic arrangements in Chapter 8. The energy stored in nuclei will come up in Chapter 21. He needs to understand (in Chapter 8) that the positions of atomic parts come from a balance of electrical forces. In the current chapter,

prepare him for later developments by stressing potential energy and its dependence on the relative positions of components in the system.

The table on Textbook p. 73 is a simple version of the law of conservation of energy. Many students have already heard that "energy is conserved." This law is no different from any other regularity. See the *Background Discussion* (p. 85) for further explanation. There is no great gain to be made by defining or stressing the law with students.

**Expt. 12, WARMING AND COOLING
BEHAVIOR OF A PURE
SUBSTANCE,**

fits here. See p. 67 in the Laboratory Guide.

Expt. 13, ENERGY NEEDED TO MELT ICE

fits here. See p. 71 in the Laboratory Guide.

Expt. 14, ENERGY OF CRYSTALLIZATION

fits here. See p. 73 in the Laboratory Guide.

5-2 Solid-Liquid Phase Changes

The change between solid and liquid brings up three questions: (1) Why do substances melt at a characteristic temperature? (2) Why is heat absorbed as a solid melts *at constant temperature*?; and (3) What is the mechanism by which a particular particle goes from the solid to the liquid phase? These questions are related to some extent, but they are often incorrectly mingled. The *Background Discussion* contains a fuller discussion (p. 85) for the related questions dealing with the liquid-vapor change. The same type of statements hold for the solid-liquid change. They can be summarized as follows:

1. The value of melting temperature is determined by a balance in the competition between energy and randomness. The energy change is easy to observe as heat is added; the randomness is shown by the sample becoming "more like a liquid"—that is, less regular.

This factor is not easy to observe and was formerly often omitted in beginning courses.

2. Heat is absorbed to provide the increase in the potential energy of the liquid particles over that of the particles in the solid.
3. Vaporization occurs when molecules having higher kinetic energy overcome the liquefying attractive forces. If evaporation takes place at constant temperature, there is no difference in the average kinetic energy of gas and of liquid—there is only a potential energy change as in item 2 above.

The model also leads naturally to the conclusion that the amount of energy involved is proportional to the number of molecules separated in vaporization or fusion, hence we specify *molar heat of fusion* (and in the next section, *molar heat of vaporization*).

5-3 Liquid-Gas Phase Changes

Use the same line of reasoning as in Section 5-2. See *Background Discussion*, p. 85. There is one point to watch in this section. Don't use a *nonequilibrium* example, such as the evaporation of water from the hand. This particular example could be confusing, because the liquid will cool as it evaporates from the hand, especially if evaporation is rapid, and an incorrect implication may be drawn. A kinetic energy change (from liquid to gas) does take place in the example cited, *but* this is not the proper point to be made, since no change in temperature occurs in an equilibrium system. The best course is to use the example of a liquid in equilibrium with its vapor in a closed system at a fixed temperature.

You may use the kinetic model to help the student rationalize the fact that the heat of vaporization, which involves large molecular separations, is greater than the heat of fusion, which involves small molecular displacements.

**Demo. 16, EQUIVALENCE OF LIQUID AND
VAPOR TEMPERATURE FOR A
BOILING SAMPLE,**

fits here. See p. 77 in the Laboratory Guide.

5-4 Vapor Pressure in Liquid-Vapor Equilibrium

The picture of an evaporating liquid developed in Section 5-3 is related to equilibrium where no measurable changes are visible. This important concept, equilibrium, will be developed in Chapter 13 and used frequently thereafter. At this point emphasize the apparent unchanging aspect of observed properties at equilibrium.

5-5 Change of Vapor Pressure with Temperature

Demo. 17, VAPOR PRESSURE OF A LIQUID AT TWO TEMPERATURES,

fits here. See p. 78 in the Laboratory Guide.

The picture of vapor pressure leads to our definition of the boiling temperature in terms of vapor pressure. (See also p. 88.)

5-6 Vapor Pressure in Solid-Vapor Equilibrium

This short section completes the "cycle" of phase changes. It is a commonly known change, but one the student probably won't recognize. In fact, you might introduce this topic (before the student reads the section) by asking "Why *is* Dry Ice dry?" Then bring the students to see that at atmospheric pressure there is no observable melting temperature. The vapor pressure of the solid reaches one atmosphere below that temperature. The phenomenon is not so rare; iodine, "mothballs," and various fumigating solids do the same.

Demo. 18, PREPARATION AND VAPOR PRESSURE OF IODINE,

fits here. See p. 80 in the Laboratory Guide.

Background Discussion

Conservation of Energy

Our treatment of the energy conservation law may be new. This important law is so well known and has such usefulness that it is often given as a dictum. Such authoritarianism is unwarranted, however, because this law evolved in the same manner as all other scientific generalizations.

Consider the totality of energy existing at some ancient time before the concept of energy was devised. All the occurrences we now describe by the law were then taking place, but there was no stated law of energy conservation. Nor was there a gas law or any other description of natural phenomena. Eventually the measuring sciences were developed, and kinetic energy was invented, at first as a mechanical idea. The next step was to divide energy into types: heat, motion of bodies, and so on. Potential energy was invented to account for stored energy. Once there were types for interconversion, a conservation law was

possible. The total quantity of energy could be broken up into man-made categories.

But these categories are neither unique nor complete. For instance, the type of energy we now call molecular vibration is a fairly recent invention. Nuclear energy is another such example. As each new kind of energy was needed to explain physical phenomena, it was fitted into the conservation pattern. Only rather recently, Einstein's relation between mass and energy has added another extension to this continuing development. Other kinds of energy will undoubtedly be proposed as the structure of the nucleus is revealed more fully.

Factors Fixing Vapor Pressure

A valid discussion of vapor pressure and its change with temperature requires the use of concepts that are introduced in Chapter 13 (*Equilibrium*). It would be premature to raise

them for discussion at this time. Keep the discussion on an empirical basis; experiment shows that the vapor pressure of every liquid increases as its temperature is raised. The following remarks give you the treatment that will be used in Chapter 13.

To understand why a liquid has a fixed vapor pressure (at a given temperature) and why the vapor pressure changes with temperature, let us consider the following system. A closed container has some liquid in equilibrium with its vapor. The temperature is kept constant, and there is nothing in the container except the substance we are studying.

The liquid contains a certain amount of total energy—call it $H(l)$. The gas contains a larger amount of energy, $H(g)$. These energy values might be related to stability. In any system, there is a tendency toward minimum energy (greatest stability). We see this tendency in operation in the condensation of a gas at its boiling temperature.

At the same time, there is a certain amount of randomness or lack of order in the liquid—call it $S(l)$ —and in the gas, $S(g)$. There is another natural tendency for a system to achieve maximum randomness. This tendency is sometimes expressed in terms of the number of ways the particles can be arranged. The random arrangements are more numerous, and thus more likely. Another way to say this is that order is not achieved without effort. Once achieved, there is a tendency for order to disappear.

From these descriptions we can consider what happens when a molecule goes from the liquid state to the gaseous state. There is a change in energy (ΔH) and a change in randomness (ΔS). These changes are the differences $H(l) - H(g)$ and $S(l) - S(g)$, and they work in opposition, the condition of lowest energy corresponding to minimum randomness. The chance for randomness goes up as the particles are farther apart and have a wider distribution of energy. But these arrangements require more energy to achieve and are less stable. It turns out that equilibrium is that condition at which these two effects are in balance, i.e., $\Delta H = T\Delta S$. Temperature is in-

cluded because of the dependence of randomness upon temperature.

When a liquid vaporizes, there is an increase in randomness as molecules enter the gas phase. As the pressure of the gas rises, however, the difference in randomness between liquid and gas decreases. The liquid continues to evaporate at constant temperature until this difference has been reduced enough such that $T\Delta S$ equals ΔH . No further pressure rise occurs at this temperature. When the temperature is raised, the balance between ΔH and $T\Delta S$ is upset again; now $T\Delta S$ is larger than ΔH . Further vaporization raises the gas pressure, lowering ΔS (difference in randomness), and the equality $\Delta H = T\Delta S$ is restored. Thus a rise in temperature must raise the vapor pressure.

Many teachers discuss the relationship between vapor pressure and temperature in terms of the cooling effect one observes when a liquid evaporates. The cooling of the remaining liquid is related to the escape of the more energetic molecules from the liquid, resulting in a net lowering of the temperature of the remaining liquid. Raising the temperature of the liquid increases the fraction of the molecules thus able to escape, hence the vapor pressure rises.

This treatment is all quite valid except for the conclusion. It is true that the more energetic molecules leave the liquid as it evaporates and that, in the nonequilibrium state that results, the liquid is somewhat cooler (this is not an equilibrium situation, because the temperature in the system is not constant throughout). It is also true that raising the temperature of the liquid increases the fraction of molecules able to escape. This will surely increase the *rate of approach* to equilibrium. It is not at all necessary on this basis that the equilibrium be shifted in favor of higher vapor pressure.

The difficulty in the argument is that kinetic observations in a system *not* at equilibrium are used to deduce conditions at equilibrium. From a kineticist's point of view, the cooling of a liquid on evaporation merely indicates that an activation energy is associated with evaporation. The lowering of the temperature gives *no* infor-

mation about the sign of ΔH .

Turning to the equilibrium situation, with the temperature uniform throughout, we note that the kinetic energy distribution among molecules in the liquid phase is *identical* to the kinetic energy distribution in the gas phase. Equal temperatures imply that the K.E. distribution is the same. Hence it is not clear whether raising the temperature (and hence the fraction of molecules with enough energy to penetrate the surface) favors liquid or gas. *Both* the liquid and the gas molecules now have more high K.E. molecules.

A valid mechanistic argument can be framed, but it must be based upon the process as it occurs at equilibrium (rather than on the behavior of a nonequilibrium system such as an evaporating liquid). Such an argument misses a valuable opportunity to expose the student to the two factors that fix *all* equilibria, the tend-

ency toward minimum energy opposed by the tendency toward maximum randomness, the latter being implemented by temperature.

It is now convenient to discuss the behavior of real gases as a modification of the PV curve for an ideal gas. If we assume relatively strong attractive forces between molecules, the processes just described give curves represented by the solid lines of Figure 5-1 (right half). The broken lines show the behavior of an ideal gas.

At point 1, deviation from the ideal curve is becoming pronounced, and at point 2, condensation of vapor begins, and continues until all of the vapor is gone (point 3). Beyond point 3, attempts to reduce the volume further simply raise the pressure of the system more rapidly because the molecules are already in contact. The line from point 3 to point 4 indicates that liquids have very low compressibility, a property which we apply in a hydraulic brake system.

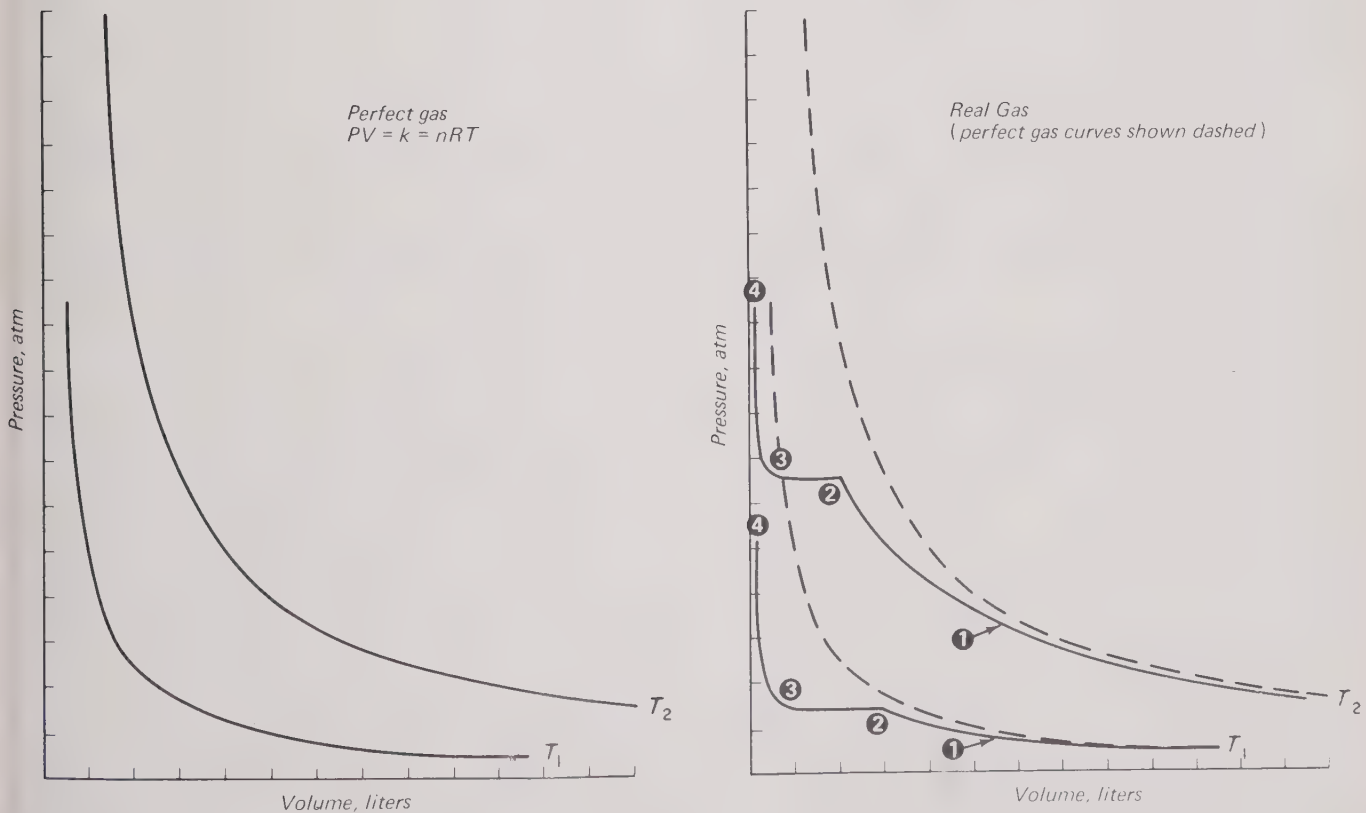


FIGURE 5-1
Pressure versus volume for gases.

If we raise the temperature of our system to T_2 , the kinetic theory tells us that the molecules are moving faster. It follows that the molecules must be brought closer together before the forces of intermolecular attraction will be strong enough to overcome the kinetic energy of the molecules and form a condensed phase. Such arguments suggest that at the higher temperature, T_2 , the liquid phase will appear at a lower volume (higher pressure) than it did at the lower temperature, T_1 . The shape of the upper curve for T_2 is then predicted by the model used, and is found experimentally.

It is gratifying to find that all of this behavior, including the rough shapes of the curves at T_1 and T_2 , is suggested by a van der Waals modification of the ideal gas equation.

This modified equation gives one way to determine the size of molecules, since the corrective factor b can be interpreted as a measure of the molecular size. We can calculate from b the radius of a sphere whose volume equals the molecular volume. The calculated value gives an estimate of the van der Waals radius of the molecule.

Before going on we should inject a final word of caution relative to the kinetic theory of liquids. Owing to difficulties introduced by molecular size and shape, because forces of intermolecular attraction are highly specific, and because motions in the liquid state are not easy to separate and identify, the detailed quantitative study of liquids is much more difficult than that of gases. Our present-day knowledge leaves much to be desired.

Vapor Pressure, Boiling and Freezing Temperatures for Pure Liquids

The arguments just considered indicate that at a given temperature, liquid and vapor can exist in equilibrium at only a single pressure (i.e., P_1 for T_1 in Figure 5-1). Note also that a change in temperature changes the equilibrium pressure (i.e., P_2 for T_2 in Figure 5-1). We should then be able to plot the pressure of the vapor-liquid

equilibrium against the temperature of the system. Such a curve is shown in Figure 5-2. It seems

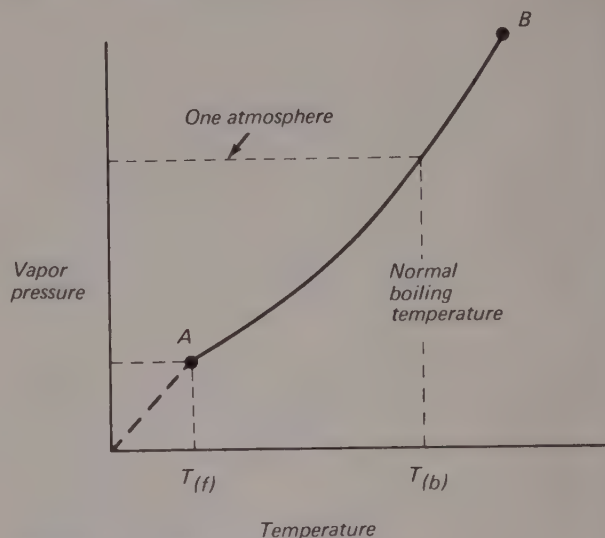


FIGURE 5-2

A generalized pressure-temperature diagram.

fairly clear that this curve should start at the freezing temperature of the liquid. Below the freezing temperature, T_f , the substance is a solid, which likewise exists in equilibrium with the vapor above it. The solid has a measurable vapor pressure, as shown by the broken line in the figure. The vapor pressure rises as the temperature is increased. The point B corresponds to the critical conditions discussed on p. 89 and below.

In several places in the Textbook and in this Guide we have casually referred to the boiling temperature. Like the burning of the candle, the concept of boiling is a common one. Perhaps we can again profit from a closer analysis of the process. Experimentally, boiling is characterized by the formation of bubbles in the liquid. (It is best if you can lead the student to a statement of this fact in class discussion.) Bubbles then rise to the surface and break. Under what conditions can such bubbles form? To answer this question consider the situation existing inside a spherical bubble in a pure liquid, depicted in Figure 5-3. The bubble, if formed from the pure liquid, contains only gaseous molecules of the pure substance. These gaseous molecules are in

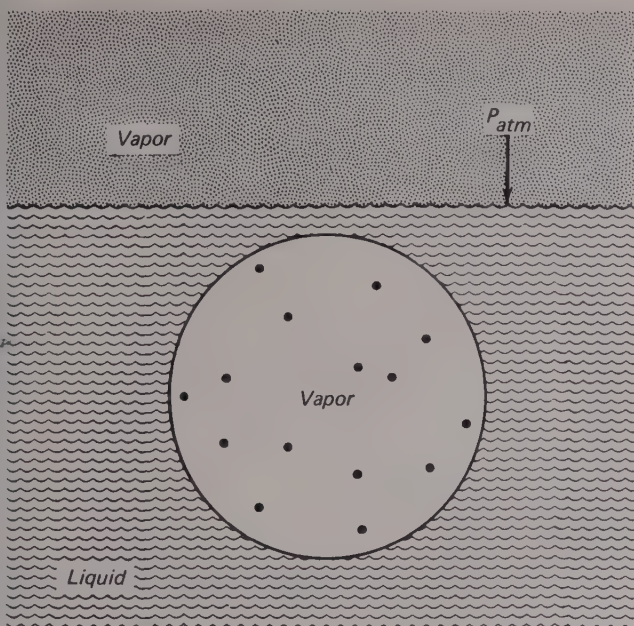


FIGURE 5-3

Bubble formation in the boiling process.

rapid random motion and exert an outward pressure on the inner surface of the bubble. This outward pressure of vapor is just balanced by the inward pressure of the liquid. Since the pressure pushing inward on a bubble just below the surface is very nearly equal to the pressure of the atmosphere above the liquid, it is convenient to define the boiling temperature as that at which the vapor pressure of the liquid is equal to the pressure above the liquid surface. At the *normal boiling temperature* the pressure above the surface is 760 mm (see Figure 5-3).

Another question is sometimes raised in discussions of boiling. Students occasionally wonder why the liquid doesn't all boil away at once when the boiling temperature is reached. This is a question about rate. The above discussion provides at least two variables of importance in considering this question. Our kinetic model of a liquid shows clearly that, in boiling, the more rapidly moving molecules leave the liquid, and that heat must be added to the liquid to accelerate the slower molecules remaining in the liquid phase. Heat transfer may be a slow process. A second variable that may retard boiling is slow nucleation, or bubble formation. The results of

this second factor may be dramatic!

If we return to the liquid-vapor pressure curve of Figure 5-2 another important question arises which some more interested students may appreciate. The following is not suitable for general class discussion. Does the vapor pressure-temperature curve continue indefinitely, or does it stop abruptly when some definite temperature is reached? Our kinetic model of a liquid provides a clear answer. As noted earlier, the major difference between a liquid and a vapor is in the number of molecules per unit of volume. As the temperature is raised, the liquid molecules vibrate more violently, and the liquid expands slightly; as a result, the number of molecules per unit of volume in the *liquid phase decreases slightly* as the temperature goes up. At the same time, an increase in temperature *increases* the number of molecules per unit of volume in the *vapor phase*, since more molecules have enough energy to overcome the intermolecular forces of attraction. At some temperature the difference between the vapor phase and liquid phase will disappear. For example, the density and surface tension of gas and liquid become the same. The liquid-vapor surface disappears, and the two cannot be detected as separate phases. The temperature at which this occurs is known as the *critical temperature* of the substance. The vapor pressure of the liquid at the critical temperature is the *critical pressure*. Our vapor pressure curve must then rise to the critical temperature and end abruptly at point *B* on Figure 5-2.

One may wonder about another facet of our example. We refer to the liquid as being under a constant pressure of 1 atmosphere, yet the vapor pressure of our liquid drops well below one atmosphere as the temperature is reduced. Molecules deep in the liquid phase cannot differentiate between pressure arising from impacts of air molecules on the liquid surface and pressure arising from impacts of molecules of our vapor. Accordingly, the bulk of the liquid behaves as though it were under a pressure of one atmosphere of pure vapor. At the liquid-vapor surface, however, the equilibrium exists only between vapor and liquid molecules; the air molecules

are unimportant to the equilibrium. For this reason, we may consider the total pressure acting on the liquid as made up of the partial pressure

of the vapor plus the partial pressure of the air above the system.

Answers to Exercises and Problems

Exercise 5-1

Calculate approximately how much energy is released when there is 1 cm of rain over an area of 10^{11} cm² (about 100 square miles). The density of water is 1 g/cm³.

Answer. 5.4×10^{10} kcal.

Answer

$$\begin{aligned} \text{moles H}_2\text{O} &= (1 \text{ cm})(10^{11} \text{ cm}^2) \left(\frac{1 \text{ g}}{\text{cm}^3} \right) \\ &\times \left(\frac{1 \text{ mole}}{18 \text{ g H}_2\text{O}} \right) = 5.6 \times 10^9 \text{ moles H}_2\text{O} \\ \text{Energy release} &= \left(9.7 \frac{\text{kcal}}{\text{mole}} \right) (5.6 \times 10^9 \text{ moles}) \\ &= 54 \times 10^9 \text{ kcal} \quad \text{or} \quad 5.4 \times 10^{10} \text{ kcal} \end{aligned}$$

Exercise 5-2

Suppose one mole of water evaporates in one day. Approximately how many molecules leave the liquid each second?

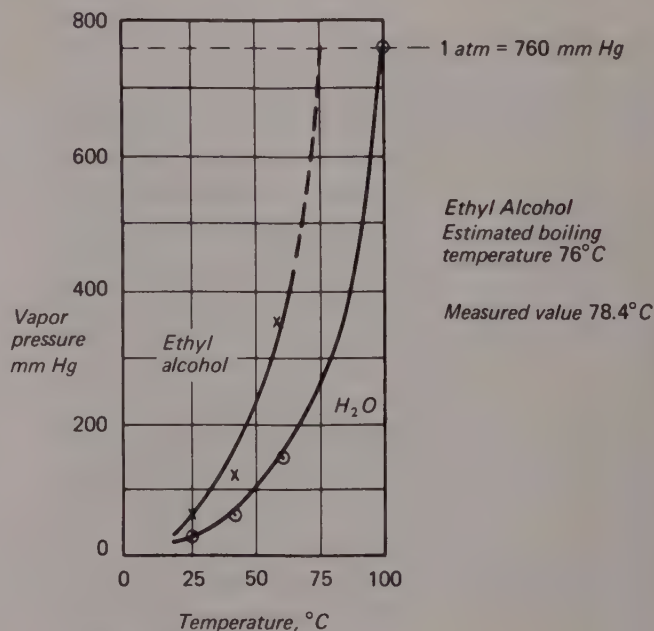
Answer

$$\begin{aligned} 1 \text{ day} &= \left(60 \frac{\text{sec}}{\text{min}} \right) \left(60 \frac{\text{min}}{\text{hr}} \right) \left(24 \frac{\text{hr}}{\text{day}} \right) \\ &= 8.6 \times 10^4 \text{ sec} \\ \frac{6.0 \times 10^{23} \text{ molecules evaporate/day}}{8.6 \times 10^4 \text{ sec/day}} \\ &= 7 \times 10^{18} \frac{\text{molecules evaporate}}{\text{sec}} \end{aligned}$$

Exercise 5-3

Compare the data for the vapor pressure of water and ethyl alcohol to estimate the boiling temperature of ethyl alcohol.

Answer



Problem 1

When a ball is thrown straight up, at what point or points in its trajectory does it have

- maximum potential energy?
- maximum kinetic energy?
- minimum potential energy?
- minimum kinetic energy?

Answer

- At the top of its flight.

- (b) At the start of the flight. If there was no air resistance, it would also have maximum kinetic energy at the end of the flight.
- (c) At the end of the flight when it is at ground level.
- (d) At the top of flight when it reverses direction.

Problem 2

Discuss the potential and kinetic energy that a skier has

- (a) as he gets aboard the ski lift.
- (b) as he travels to the top of the ski slope.
- (c) as he skis down the hill and reaches the bottom of the ski slope.

Answer

	Potential Energy	Kinetic Energy
(a)	zero or nearly so	medium
(b)	increasing	medium
(c)	decreasing	can be high or low, depending on how he takes the slope.

Problem 3

Discuss the various kinds of energy involved when you ride an elevator to the tenth floor of an office building.

Answer

As you walk into the elevator, you have low potential energy but some kinetic energy of walking. You push the button and momentarily potential and kinetic energy are low. As a result of the electrical connections, the potential energy represented by separation of charge in the wires is converted, in a motor, to kinetic motion of the motor. It turns and pulls the elevator up; thereby its energy is divided. Some becomes kinetic energy of the moving elevator, and some potential energy as the elevator is separated from ground level. When the tenth floor is reached, the car stops. You walk off using the kinetic energy generated by muscle action to carry some potential energy off the elevator.

Problem 4

A dam, such as the Hoover Dam on the Colorado River, stores water. It also can be said to store energy. Explain.

Answer

The dam stores energy by holding water at a

level above that which it would naturally take. A ledge holding a rock is also storing energy, but not in an arrangement that lends itself to extracting the energy. Water behind a dam is easy to control in its "fall" so that use can be made of its potential energy.

Problem 5

How much heat energy must be removed to freeze an ice tray full of water at 0°C if the ice tray holds 540 grams of water? What happens to this heat energy?

Answer

$$\left(\frac{540 \text{ g H}_2\text{O}}{18 \text{ g/mole}}\right) \left(\frac{1.44 \text{ kcal}}{\text{mole}}\right) = 43.3 \text{ or } 43 \text{ kcal to be removed}$$

The heat energy is pumped out of the refrigerator and into the room.

Problem 6

Compare the potential energy of 10 grams of solid water and 10 grams of liquid water, both samples at 0°C.

Answer

Energy must be added to ice to make liquid. The temperature is constant; so this energy is present as potential energy.

Problem 7

A metal cylinder, initially at 25°C, is placed in an insulated cup containing water and crushed ice. After the system has come to thermal equilibrium, there is ice remaining.

- (a) What is the equilibrium temperature of the metal cylinder?
- (b) What happens to the energy given up by the metal cylinder?
- (c) If 20 grams of ice were melted, how much energy was given up by the cylinder?

Answer

- (a) 0°C.
- (b) It goes to melt some ice.

$$\left(\frac{20 \text{ g ice}}{18 \text{ g/mole}}\right) (1.44 \text{ kcal/mole}) = 1.6 \text{ kcal given up.}$$

Problem 8

When the temperature drops below 0°C, the fruit on the trees in an orchard can sometimes be protected by flooding the orchard. Why?

Answer

The water is cooled by the air until it is at 0°C; then the heat of fusion must be removed to freeze the water. If the air is still, it will be warmed by the removed heat. The net result can be a balance in which water, air, and, hence, fruit is at about 0°C rather than being at some lower temperature which would freeze the fruit.

Problem 9

In an experiment, 100 grams of water at 80°C is allowed to interact with ice (at 0°C). Enough ice is used to cool the water to 0°C. The ice and water are placed in an insulated container so that all the energy given up by the water melts ice. After the system reaches equilibrium at 0°C, there are 200 grams of liquid water present.

- How much ice is melted?
- How much energy is given up by the 100 grams of water in cooling from 80°C to 0°C?
- How much energy is required to melt 1.0 gram of ice?
- How much energy is required to melt 1.0 mole of ice?

Answer

- 100 g
- (80C° change in temp.)

$$\times \left(\frac{1 \text{ cal}}{\text{g-deg}} \right) (100 \text{ g}) \left(\frac{1 \text{ kcal}}{1000 \text{ cal}} \right) = 8 \text{ kcal}$$

$$(c) \frac{8 \text{ kcal}}{100 \text{ g ice melted}} = 0.08 \text{ kcal/g ice melted}$$

$$(d) (0.08 \text{ kcal/g}) (18 \text{ g/mole}) = 1.44 \text{ or } 1.4 \text{ kcal/mole}$$

Note: The point of this problem is to work out the value for molar heat of fusion from experimental data, not to use the value 1.44 in calculation.

Problem 10

What amount of ice must be added to 540 grams of water at 25°C to cool the water to 0°C and have no ice remaining?

Answer

$$\begin{aligned} (540 \text{ g H}_2\text{O}) \left(\frac{1 \text{ cal}}{\text{g-deg}} \right) (25 \text{ C}^\circ \text{ change}) \\ = \left(\frac{x \text{ grams ice}}{18 \text{ g/mole}} \right) \left(1440 \frac{\text{cal}}{\text{mole}} \right) \\ x = \frac{(540)(18)(25)}{1440} = 168, \text{ or } 170 \text{ g ice needed.} \end{aligned}$$

Problem 11

A liquid is heated at its boiling temperature. Although energy is added to the liquid, its temperature does not increase. Explain.

Answer

Heat is needed to vaporize a liquid; hence a gas has more energy than the liquid from which it comes. As a liquid boils, the energy put in (as heat) is used to separate the molecules of the liquid instead of to raise the temperature.

If you wish to anticipate Chapter 11, you might mention that the liquid has lower energy than the gas because the molecules attract each other. Hence the heat of vaporization increases the *potential energy* of the molecules as they enter the gas phase. It is incorrect to say that the heat of vaporization increases the kinetic energy of the molecules as they vaporize, since the liquid and vapor are at the same temperature, hence their molecules possess the *same* kinetic energy distribution.

Problem 12

What is the maximum amount of heat energy that you can lose as one gram of water evaporates from your skin?

Answer

Water, as it vaporizes, absorbs 10 kcal/mole. Therefore

$$1 \text{ g} \times \frac{1 \text{ mole}}{18 \text{ g H}_2\text{O}} = 0.056 \text{ mole}$$

$$0.056 \text{ mole} \times \frac{10 \text{ kcal}}{\text{mole}} = 0.56 \text{ kcal}$$

Problem 13

Which is more likely to cause a severe burn, one gram of H₂O(g) at 100°C or one gram of H₂O(l) at 100°C?

Answer

The gas. It would give up heat as it cooled down, just as the water sample would; in addition, the gas would release the heat of liquefaction.

Problem 14

Liquids used in rocket fuels are passed over the outer wall of the combustion chamber before being fed into the chamber itself. What advantages does this system offer?

Answer

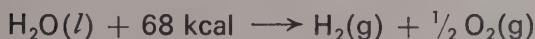
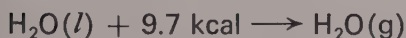
- The chamber walls are cooled as the liquid vaporizes, thereby extending their life.
- The heat absorbed causes the liquid fuel to vaporize, which is desirable for combustion. The vapor burns more rapidly than the liquid, and potentially useful energy is not consumed in the combustion chamber to vaporize the liquid.

Problem 15

Which requires more energy, vaporizing one mole of liquid water or decomposing one mole of water by electrolysis? Explain.

Answer

Note that (a) vaporizing is a phase change and that (b) decomposing is a chemical reaction, characterized by larger heat effects. In (a) water molecules are merely being separated from each other. In (b) water molecules are being separated into atoms, breaking bonds. The heats of (a) and (b) can both be obtained from the Textbook; the heat of vaporization can be found in Section 5-3, and the heat of decomposition is the opposite of the heat of formation, given in Section 3-1.

**Problem 16**

Suggest possible explanations for the regularity between boiling temperature and molar heat of vaporization for the liquids given in Table 5-2.

Answer

The boiling temperature goes up when stronger

forces hold the molecules together. For the same reason, a larger amount of energy is needed to vaporize the liquid. Table 5-2 is on p. 76 (Text).

Problem 17

Two of the methods suggested for conversion of seawater to fresh water are evaporation or freezing of water. Which process uses more energy?

Answer

Freezing requires removal of 1.44 kcal/mole. Boiling needs 9.7 kcal/mole input once the water is at 100°C. Freezing is probably cheaper.

Problem 18

Because of its excellent heat conductivity liquid sodium has been proposed as a cooling liquid for use in nuclear power plants.

- Over what temperature range could sodium be used in a cooling system designed to operate at one atmosphere pressure?
- How much heat would be absorbed per kilogram of sodium to melt the solid when the cooling system is put in operation?
- How much heat would be absorbed per kilogram of sodium if the temperature rose too high and the sodium vaporized? Use the data in Tables 5-1 and 5-2.

Answer

- 98–889°C. The lower temperature limit is fixed by the point at which the coolant freezes (98°C); and the upper limit, by the temperature at which the vapor pressure reaches 1 atmosphere, the boiling temperature (889°C).

- The number of moles in one kilogram is

$$\frac{1000 \text{ g}}{23.0 \text{ g/mole}} = 43.5 \text{ moles}$$

The heat necessary to melt 43.5 moles of Na(s) is

$$\left(43.5 \frac{\text{moles}}{\text{kg}}\right) \left(0.63 \frac{\text{kcal}}{\text{mole}}\right) = 27 \frac{\text{kcal}}{\text{kg}}$$

- The heat necessary to vaporize 43.5 moles of Na(s) is

$$\left(43.5 \frac{\text{moles}}{\text{kg}}\right) \left(24.1 \frac{\text{kcal}}{\text{mole}}\right) = 1050 \frac{\text{kcal}}{\text{kg}}$$

Problem 19

Water is commonly used as a cooling agent in power plants. Repeat Problem 18, using one kilogram of water instead of sodium. Contrast the results for these two coolants.

Answer

(a) 0° – 100°C . Whereas sodium is useful over almost 800°C , water is useful over only 100°C . It is a disadvantage, however, that sodium freezes when the power plant is turned off and the temperature drops to room temperature.

(b) The number of moles in one kilogram is

$$\frac{1000 \text{ g}}{18 \text{ g/mole}} = 55.5 \text{ moles}$$

The heat necessary to melt 55.5 moles of ice is

$$\left(55.5 \frac{\text{moles}}{\text{kg}}\right) \left(1.44 \frac{\text{kcal}}{\text{mole}}\right) = 80 \frac{\text{kcal}}{\text{kg}}$$

It took only 27 kcal to melt the sodium. Notice that this heat must be put in to "start" the sodium cooling system because the sodium solidifies on "shutdown." The water would not freeze on "shutdown."

(c) The heat necessary to vaporize 55.5 moles of water is

$$\left(55.5 \frac{\text{moles}}{\text{kg}}\right) \left(9.7 \frac{\text{kcal}}{\text{mole}}\right) = 538 \frac{\text{kcal}}{\text{kg}}$$

This is about one-half the heat that would be absorbed by vaporizing an equal mass of sodium.

Problem 20

How many grams of ice could be melted by the energy obtained as 18.0 grams of steam is condensed at 100°C and cooled to 0°C ? How does the amount of energy obtained as the steam condenses compare to the amount of energy released as the same water is cooled from 100°C to 0°C ?

Answer

$$\left(\frac{18.0 \text{ g H}_2\text{O(g)}}{18.0 \text{ g/mole}}\right) \left(9.7 \frac{\text{kcal}}{\text{mole}}\right) = 9.7 \text{ kcal obtained at condensation}$$

$$(18.0 \text{ g H}_2\text{O(g)}) (100^{\circ}\text{C change}) \left(\frac{1 \text{ cal}}{\text{g-deg}}\right) \times \left(\frac{1 \text{ kcal}}{1000 \text{ cal}}\right) = 1.8 \text{ kcal released on cooling}$$

The heat removed by condensation is much greater than that from cooling.

Total energy available to melt ice = 11.5 kcal

$$\left(\frac{\text{g ice melted}}{18.0 \text{ g/mole}}\right) (1.44 \text{ kcal/mole}) = 11.5 \text{ kcal}$$

$$\text{ice melted} = \frac{(11.5)(18)}{1.44} = 144, \text{ or } 140 \text{ g}$$

Problem 21

A sample of steam at 100°C is condensed to give 180 grams of water, also at 100°C . All of the heat energy is used to vaporize benzene (C_6H_6). This procedure yields 1030 grams of gaseous benzene at its boiling temperature.

- Is the molar heat of vaporization of C_6H_6 greater or less than that of H_2O ?
- What is the value for the molar heat of vaporization for benzene?

Answer

$$(a) \left(\frac{1030 \text{ g benzene}}{78 \text{ g/mole}}\right) = 13.2 \text{ moles benzene}$$

$$\left(\frac{180 \text{ g H}_2\text{O}}{18 \text{ g/mole}}\right) = 10 \text{ moles H}_2\text{O}$$

The same amount of heat vaporizes more moles of benzene (13.2) than water (10). Therefore the molar heat of vaporization is *less* per mole of benzene.

$$(b) (10 \text{ moles H}_2\text{O})(9.7 \text{ kcal/mole}) = 97 \text{ kcal obtained from H}_2\text{O}$$

$$(13.2 \text{ moles benzene})(\Delta H_{\text{vap}}) = 97 \text{ kcal}$$

$$\Delta H_{\text{vap}} = 7.3 \text{ kcal/mole benzene}$$

Problem 22

Why is the boiling temperature for water lower at Denver, Colorado (altitude: 5280 feet) than in Boston, Massachusetts (at sea level)?

Answer

At the higher altitude of Denver, Colorado, atmospheric pressure is much lower (about 630 mm) than at sea level (about 760 mm). Since any liquid boils at a temperature for which its vapor pressure equals the surrounding (atmospheric) pressure, a lower vapor pressure is needed for boiling in Denver, Colorado. Since the vapor pressure of all liquids increases as the temperature is raised, a lower temperature is needed to boil water in Denver (in fact, it boils at a temperature near 95°C).

Problem 23

Both carbon tetrachloride, CCl_4 , and mercury, Hg, are liquids whose vapors are poisonous to breathe. If CCl_4 is spilled, the danger can be removed merely by airing the room overnight. If Hg is spilled, it is necessary to pick up the liquid droplets with a "vacuum cleaner" device. Explain.

Answer

Carbon tetrachloride has a high vapor pressure (100 mm at 23°C). Hence "airing" the room overnight permits the CCl_4 to evaporate and be removed. The mercury has such a low vapor pressure (10^{-3} mm at 25°C) that it evaporates very slowly. Droplets of mercury, and the consequent danger of poisoning, would remain after many weeks of "airing" the room.

Problem 24

How would the vapor pressure of water measured at 100°C on the moon compare to the vapor pressure of water at the same temperature here on earth?

Answer

The vapor pressure of water at 100°C on the moon would be the same as on earth or any other place. However, some device would be needed to maintain the 760 mm. The lack of an atmosphere on the moon means water would boil at a very low temperature unless the water was in a closed container.

Problem 25

Explain why it is that leftover food placed in a refrigerator tends to dry out if left uncovered.

Answer

Water has a vapor pressure at all temperatures. The vapor is continually removed by freezing on the coils. Thus, more water evaporates from the food in an attempt to achieve the equilibrium value of vapor pressure.

Problem 26

Why do some food production processes, such as the refining of sugar, make use of low pressure evaporation?

Answer

Low pressure evaporation allows use of a low temperature. Sugar, and other foods, are not damaged by the low temperature but could not stand the heating necessary to evaporate the water quickly at one atmosphere.

Problem 27

The vapor pressure of a liquid increases as the temperature increases. State two causes for the increase in vapor pressure.

Answer

Increased temperature means greater kinetic energy of the molecules on the average. As a result, more molecules will go into the vapor phase and they will be traveling faster. Both effects will contribute to increase vapor pressure.

Problem 28

In an experiment, a 500 ml round-bottom flask was filled half-full with water. The water was heated and boiled for a few minutes filling the flask with water vapor. The flask was stoppered and quickly cooled under a stream of cold water. Explain why the water boiled as the flask was cooled.

Answer

As the flask was cooled the gaseous water condensed, producing a low pressure over the liquid water. The vapor pressure of the warm water was greater than the low pressure produced so boiling occurred. A liquid boils when its vapor pressure is equal to (or greater than) the opposing pressure.

Problem 29

A one gallon can containing a small amount of water was heated. After the water had been boiling for a few

minutes, to fill the can with water vapor, a stopper was used to seal the can. The can was then cooled and it collapsed. Explain.

Answer

The cooling water caused the gaseous water in the can to condense, producing a low pressure. The walls of the can were not strong enough to stand the pressure difference between the atmosphere (about 760 mm Hg) on the outside and the low pressure (30–60 mm Hg) on the inside.

Some students may ask why the flask in Problem 5-28 didn't break when the same experiment

was done. The flask walls are thicker, and they are strong enough to take the pressure difference.

Problem 30

Name two solids that have a high enough vapor pressure at room temperature that you can detect their presence by smell.

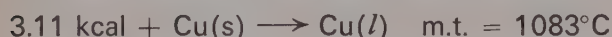
Answer

Mothballs (naphthalene or *paradichlorobenzene*), camphor, cedar wood (odor is from natural oils in the wood), iodine.

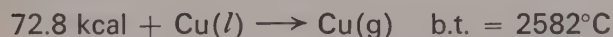
Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

Questions 1 and 2 refer to an experiment in which solid copper is heated to melting.



The liquid copper is heated until it is changed into vapor.



1. How much heat is required to melt 6.35 g of Cu?

Answer: 311 cal.

2. How much heat is required to vaporize 6.35 g of Cu?

Answer: 7280 cal.

Consider the system described below in answering questions 3–5.

A flask is half full of 1.00 *M* sodium carbonate, Na_2CO_3 , solution with solid water (ice) floating in the solution. The system has been standing long enough for equilibrium to have become established. The flask is stoppered.

3. How many phases are present in the entire system? (Neglect the flask and stopper.)

Answer

Three. They are (1) the gas phase above the liquid; (2) the solid water; and (3) the salt solution.

4. Which of the phases present is a pure substance?

Answer: Solid water.

5. How many grams of Na_2CO_3 are dissolved in 500 ml of the 1.00 *M* solution?

Answer

A 1.00 *M* solution of Na_2CO_3 contains 106 g/liter.

$$\frac{106 \text{ g}}{\text{liter}} \times 0.5 \text{ liter} = 53 \text{ g}$$

The next two questions refer to this experiment.

A heavy wall flask is partially evacuated to 500 mm Hg pressure of air. A small amount of benzene is introduced into the flask in order that some liquid will remain after equilibrium has been established. The vapor pressure of benzene at room temperature, 21°C , is about 80 mm Hg.

6. If a little more benzene (negligible volume change) is added to the flask, how will this affect the total pressure of the system?

Answer

The total pressure of the system will remain essentially unchanged.

7. If the temperature of the system is increased, what will happen to the pressure? Why?

Answer

It will increase because the air pressure and vapor pressure increase on heating.

8. Describe the various energy conditions of a badminton shuttlecock as it is served, strikes the net, and comes to rest on the court.

Answer

The shuttlecock is given potential energy (above the court) as it is raised, and kinetic energy is imparted by the racquet. As it flies to the net, potential energy may be going up (if it is rising) or down. Some energy is lost

because of air friction. At the net the majority of kinetic energy is transferred to the net. Finally, the remaining potential energy is lost as the shuttlecock reaches the court surface.

9. Select the FALSE statement from the following series about a liquid which is boiling :

- (a) Bubbles form rapidly.
- (b) Vapor pressure must be 760 mm Hg.
- (c) Liquid and gas have the same temperature.
- (d) Heat is absorbed by the liquid without a change in temperature.
- (e) Vapor is forming.

Answer

(b) is false. The vapor pressure equals the opposing pressure and can have a wide range of values.



Intent and Approach

This chapter is used to introduce four major topics:

properties of solutions,
the electrical nature of matter,
the kinds of compounds that are electrolytes,
and
solubility.

Each topic has some important concepts that will be carried on through the course. Solutions differ from pure substances, in ways dependent upon the solute and its concentration. The way of expressing concentration is important and limited to molarity in this book. The attraction between oppositely charged particles is a corner-

stone of atomic structure and chemical bonding. Here the first ideas are to be firmly planted. Something of the nature of ionic substances follows naturally after the electrical properties are understood. You should stress the individual character of ions. That is, they are not "almost like" their parent element, with just a charge to distinguish them. They are entirely separate chemical species. And as such their properties are not dependent upon the source compound. Finally, solubility is a matter of practical importance in analysis, and in the production of chemicals. It also will serve later to illustrate equilibrium calculations.

Outline

After discussion of homogeneous and heterogeneous systems, some aspects of gaseous, liquid, and solid solutions are given.

Phase changes of solutions are discussed (6-1).

Molar concentration is used for quantitative description of solution concentration (6-2). Solubility is introduced as the limit of dissolving capacity (6-3).

The different types of solutions formed by sugar and sodium chloride (6-4) lead to study of electric charge (6-5).

The electron-proton concept is used to expand

the particle model (6-6).

On the basis of atomic structure containing positive and negative charges, the electrical properties of condensed phases are explained. Ions are introduced (6-7) and shown to have a part in some solids (6-8).

The types of compounds that provide ions in solution are classified as acids, bases, and salts (6-9).

Some general rules of electrolyte solubility are presented (6-10).

A review (6-11) summarizes.

New Concepts

1. Solutions act differently from pure substances.
2. Molar concentration.
3. The nature of solutions—especially of electrolytes.
4. The electrical properties of matter; electrons and protons.
5. Solubility and some guidelines to slightly soluble compounds.

SCHEDULE AND RELATED MATERIAL

Suggested Time : 8 days

Text Section	Topic and Other Work	Exercises	Problems				
			Easy	Medium	Hard		
6-1	Expt. 15. Cooling Behavior of a Solution	1-3	1, 2, 5	3, 4	9		
	Solution Behavior during Phase Changes						
	Expt. 16. Formula of a Precipitate						
6-2	Concentration of Solutions		6	7, 8		9	
6-3	Solubility		10-12				
	Demo. 19. Models of Relative Solubility						
	Demo. 20. Solubility vs. Temperature						
6-4	Variations of Solution Properties		13				
6-5	Electric Charge		4, 5	14		15, 16	17
	Film: Electric Interactions in Chemistry						
6-6	Electron-Proton Model			18, 19			
6-7	Electric Properties of Condensed Phases	21, 24		22, 25	23, 26		
	Demo. 21. Electrical Conductivity						
	Expt. 17. Reaction of Ions						
6-8	Ionic Solids	4, 5		20			
	Demo. 22. Solvent Effect on Conductivity						
6-9	Electrolytes		27, 28				
	Demo. 23. Conductivity of Acids, Bases, and Salts						
6-10	Solubility of Ionic Compounds		32, 33	29, 34, 35, 37, 38	30, 31, 36		
6-11	Expt. 18. Types of Solutions Review						

Development

The introductory page of this chapter defines homogeneous and heterogeneous and gives some examples of solutions in each of the phases. Liquid solutions, mainly of solids in water, are

the most commonly used in this course. The words *solute* and *solvent* cause some trouble. Assume that students generally know a solvent dissolves something.

Display samples of granite and of crystalline quartz or some other mineral. (Both can be found in nature or obtained from a mineral shop or scientific supply house.) Also display salt crystals, water, glycerin, salt water, and a mixture of salt and sand. Use these samples to point out the meaning of *heterogeneous* and *homogeneous*, *phase*, *system*, and *pure substance*.

The following examples of solutions may be helpful.

1. *Gaseous solutions*: any mixture of gases, such as air (with or without water vapor), automobile exhaust, oxygen-acetylene used in welding torches, oxygen-helium for divers.
2. *Solid solutions*: coin silver, sterling silver, commercial aluminum contains the element gallium in solid solution, silver and gold form solid solutions in all proportions.
3. *Liquid solutions*: many examples, such as carbonated drinks (gas in liquid); gasoline, whiskey, antifreeze in water (liquid in liquid); sugar or salt in water (solid in liquid).

Expt. 15, COOLING BEHAVIOR OF A SOLUTION,

fits here. See p. 82 in the Laboratory Guide.

6-1 Behavior of Solutions during Phase Changes

The experimental criteria for differentiating between a pure substance and a solution can be discussed best by illustration. Obtain data similar to that shown in Figure 6-1 (Textbook) for pure water and also for a solution of salt in water or glycerin in water. If samples of pure water and of a glycerin solution are placed in the freezing compartment of a refrigerator overnight, you can also demonstrate purification by crystallization, since the ice crystals coming out will be pure water coated with the glycerin solution. Distillation can be easily demonstrated.

You can start an interesting philosophical discussion with your class relative to the question of purity. When is water pure? How do we tell? Is the same water pure if we use a more sensitive

test for impurities? What is meant in advertisements listing a product as 99% pure? Pure what? By what test? Is it important to be so pure? Refer again to Section 1-8 on uncertainty.

The liquid-solid phase change (freezing) also serves to show differences in solution behavior from that of pure substances. Crystallization is a very common way to purify chemicals. Text Figure 6-3 illustrates.

Expt. 16, FORMULA OF A PRECIPITATE,
fits here. See p. 87 in the Laboratory Guide.

6-2 Expressing the Composition of Solutions

There are several ways to express the concentration of a solution. For this course a single method is used. It is simple and is connected to the mole method of solving quantitative problems. For this reason, express all concentrations in molarity. Develop terminology as a matter of utility, not as an end in itself. If you make sure the student understands how a 1 *M* solution is made, he will probably remember it more easily than as a word definition. This is the purpose of Textbook Figure 6-4.

6-3 Solubility

The purpose of this section is to develop a quantitative feeling about solubility. Make sure the idea of saturation is clear. The student will need this immediately for laboratory work dealing with precipitates, and will need it later for the study of equilibrium and solubility product. Chapter 13 will enlarge on this topic through the use of equilibrium concepts, but the groundwork starts here.

Notice that we have avoided using the word "insoluble." This word is too absolute and defeats one concept we wish emphasized in Chapter 13 and thereafter—that every reaction in a closed system establishes an equilibrium. Thus every substance "dissolves" to some extent. Many things, of course, do not dissolve to any appreciable extent, but the phrase "negligible solu-

bility" indicates we have neglected something, however small.

**Demo. 19, MODELS TO SHOW SOME
RELATIVE SOLUBILITIES,**

fits here. See p. 92 in the Laboratory Guide.

Demo. 20, SOLUBILITY vs. TEMPERATURE,

fits here. See p. 92 in the Laboratory Guide.

**6-4 Variations Among the Properties
of Solutions**

This section begins the presentation of the electrical nature of matter by establishing conductivity as a property of solutions. The first point is that solubility varies in a given solvent and for different solids in the same liquid. Then conductivity is brought in as a classifying test. Some solutions conduct and some do not. This sets the stage for the several following sections on the electrical nature of matter. These sections may seem to be a diversion if the student is not definitely aware of the need for knowing about the close relation of electric charges to chemically interesting solutions.

The student's experience with electrical charge is brought to his attention through the list he is asked to make near the end of this section. It is not important that the student list all the examples given, but he should now be more aware of the widespread occurrence of electrical phenomena within his own experience.

6-5 Electric Charge

Many students will know that "unlike charges attract." This section is to make sure. The action of charged bodies can be shown. The film "Electric Interactions in Chemistry" does this well and by-passes the troubling fact that local laboratory conditions often make a class demonstration difficult. The film develops Coulomb's law. We do not use the law, but we do want the student to know that force varies with distance. The film also shows some chemical

consequences of oppositely charged ions attracting each other (precipitation). Preview the film and decide what portion you want to use. See back of this book for details on ordering films.

**Film, ELECTRIC INTERACTIONS IN
CHEMISTRY,**

fits here. See p. 103 in this guide.

6-6 The Electron-Proton Model

Some students may feel the Textbook is quite cautious. They "know" atoms are made of electrons and protons and other wondrous particles; why all the fuss about it? Usually the question "How do you know atoms contain protons?" receives either no answer at all or a reply such as "So-and-so told me." You are then in a position to develop the concept. Employ any useful information the students give.

At this stage only two ideas are needed. There are the same number of protons and electrons in a neutral atom *and* the electrons can be removed to form ions. Do not go into more detail now.

**6-7 Electric Properties of
Condensed Phases**

Introduce this section with a demonstration of conduction by solutions.

Demo. 21, ELECTRICAL CONDUCTIVITY,

fits here. See p. 93 in the Laboratory Guide.

Ion and the special forms cation and anion represent new words and new concepts. They need emphasis so that the student is aware that an important idea is contained in the term ion.

There may be questions about the location of the charge and why some substances give ions in solution whereas others do not. These questions are better postponed until the chapters on energy, structure, and bonding are reached. In particular, all discussion must be delayed until Chapter 9, where atomic structure is presented.

The term (aq) is introduced, and this is a

good time to review the other symbols for state: (g), (l), and (s). These will be used considerably throughout the course for several reasons.

1. They help make the equation a more adequate description of nature.
2. They focus attention on molecular surroundings and on the fact that some properties depend upon the surroundings. This is particularly true for ions and for the term (aq), which is later used to suggest the ionic hydration sphere.
3. They are needed in Chapter 11, where the energy of a reaction depends on the state of the reactants and products.
4. They help put across the idea of "spectator ions" (those which are *not* reacting) and why they can be omitted from equations.

Emphasis on the importance of these symbols, combined with their regular use on your part, will pay off in later chapters.

Expt. 17, REACTIONS BETWEEN IONS IN AQUEOUS SOLUTION,

fits here. See p. 95 in the Laboratory Guide.

6-8 Ionic Solids

Emphasize that we are packing together spherical ions in a relatively simple geometrical arrangement. Display a model of an NaCl crystal. Make sure the student understands that individual NaCl molecules do not exist in the solid state. This is the reason the term empirical formula is introduced. NaCl represents only the ratio of atoms present. Ionic solids do not have molecular units to the extent found for covalently bonded substances.

Demo. 22, SOLVENT EFFECT ON CONDUCTIVITY,

fits here. See p. 99 in the Laboratory Guide.

6-9 Types of Compounds That Are Electrolytes

Demo. 23, CONDUCTIVITY OF ACIDS, BASES, AND SALTS,

fits here. See p. 100 in the Laboratory Guide.

This section serves to introduce the terms acid, base, and salt. These words and compound types are needed in the laboratory work. Do not spend a great deal of time now on definitions or experimental evidence. Save that for Chapter 14. Have the student understand that acids react with bases and that all three classes give conducting solutions. Do not stray off into nomenclature, valency, or oxidation number at this point.

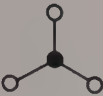
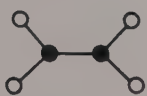
An important concept to stress here is that the ion is a separate chemical entity. Emphasize that its properties differ completely from those of the materials from which it comes. This can be related to the use of Ba^{2+} (from several sources) as a test for SO_4^{2-} , or of Ag^+ for Cl^- . This point can be quickly and effectively made by demonstrating a few precipitations.

Teachers who have struggled in the past with the attempt to make somewhat fine distinctions between the terms ionization and dissociation will appreciate the emphasis on the two major ways in which ions in solution can and do arise. This has been done without introducing new and unnecessary terms.

It is sometimes (erroneously) concluded that a substance which forms an ionic solution in water also forms an ionic solid. The HCl example is given specifically to show this isn't true. You can rely fairly well on the converse, however; an ionic solid will form an ionic solution.

This is probably a good place to discuss polyatomic ions. Describe one as a charged group of atoms which remain together. They can carry either a positive or negative charge, and the student has seen a number of examples already. The most common are listed at the top of the next page, together with their shapes. The student isn't ready for much information on bonding or structures yet.

POLYATOMIC IONS

ION	BONDING FORMULA	SHAPE
OH^- , CN^-		Linear
SCN^-		Linear
NO_3^- , CO_3^{2-}		Planar, equilateral triangle
H_3O^+		Presumed to be pyramidal
SO_4^{2-} , PO_4^{3-} ClO_4^- , NH_4^+		Tetrahedral
$(\text{OOC}\text{COO})^{2-}$ oxalate ion		Each —C—O^- =O is a planar, equilateral triangle,

6-10 Solubility of Ionic Compounds

This material should be presented as the result of many experiments such as Experiment 17. Solubility rules are not mysterious laws to memorize, but provide a convenient way to express a multitude of experiments. For instance, Textbook Table 6-2, if applied to all the metallic elements (roughly 80), gives a guide to the solubility of about 900 compounds. Even if we consider only the twenty most common metals, the table correlates the behavior of over 200 compounds. In Experiment 17 the student observed only 6 (or 12) compounds. Emphasize that this is an example of the usefulness of a generalization. The figures show how the solubilities of several common anions are related to the Periodic Table.

Expt. 18, TYPES OF SOLUTIONS,

fits here. See p. 101 in the Laboratory Guide.

Supplementary Material

Film

For ordering information see the *List of Film Sources* at the back of the Teacher's Guide.

ELECTRIC INTERACTIONS IN CHEMISTRY

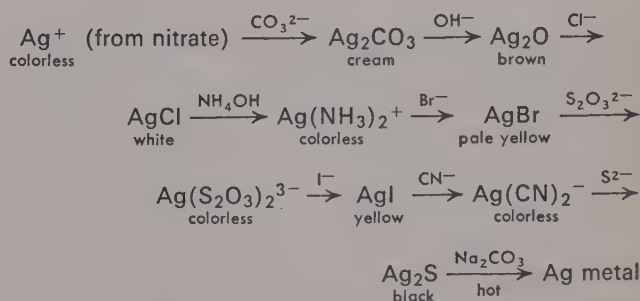
A CHEM Study film, 1963
16 mm—color

Running Time: 21 minutes

This film, prepared by Professor J. L. Hollenberg of the University of Redlands and Professor J. A. Campbell of Harvey Mudd College, illustrates the principles that opposite charges attract, like charges repel, and uncharged bodies have no electric interaction. The effect of distance on electric force is shown by a sensitive balance measuring the force between two charged spheres. The distance is varied, and the force is calculated from changes in balance readings. A graph of electric force against distance suggests the equation $F/r^2 = k$ (a constant), and the tabulated data confirm this relation. Some chemical applications of these principles are indicated by animated scenes of the migration of positive and negative ions and their mutual precipitation.

Solubility Review

In *J. Chem. Education*, **36**, 45 (1959), J. R. Schwenk gives a series of reactions showing solubility behavior of silver compounds. The series takes this course:



You can use this as a review. You should, however, skip lightly over the three complex ions. We will study them in Chapter 20.

Background Discussion

The Physical Properties of Solutions

The simple phase diagram in Figure 5-2 (p. 88) for a pure substance can serve as a starting point for a discussion of the physical properties of solutions. Let us assume that the pure substance of the figure is the solvent for our solution and that some of our solvent molecules are replaced by molecules of a nonvolatile solute such as sugar. The number of solvent molecules that can then escape from a given area of solution surface in unit time will be reduced. One of the prime reasons for this reduced rate of evaporation is the smaller number of solvent molecules per unit volume; the differences in intermolecular

attraction caused by such a change lead to a reduction of the concentration of molecules in the vapor phase and a drop of the vapor pressure of solvent above the solution. The result is shown graphically in Figure 6-1.

The model suggests quantitatively that the vapor pressure of the solvent above the solution would be directly proportional to that fraction of the total number of molecules which is solvent. Such a relationship, known as Raoult's Law, describes with fair accuracy the behavior of a relatively large number of solutions, but there are many exceptions.

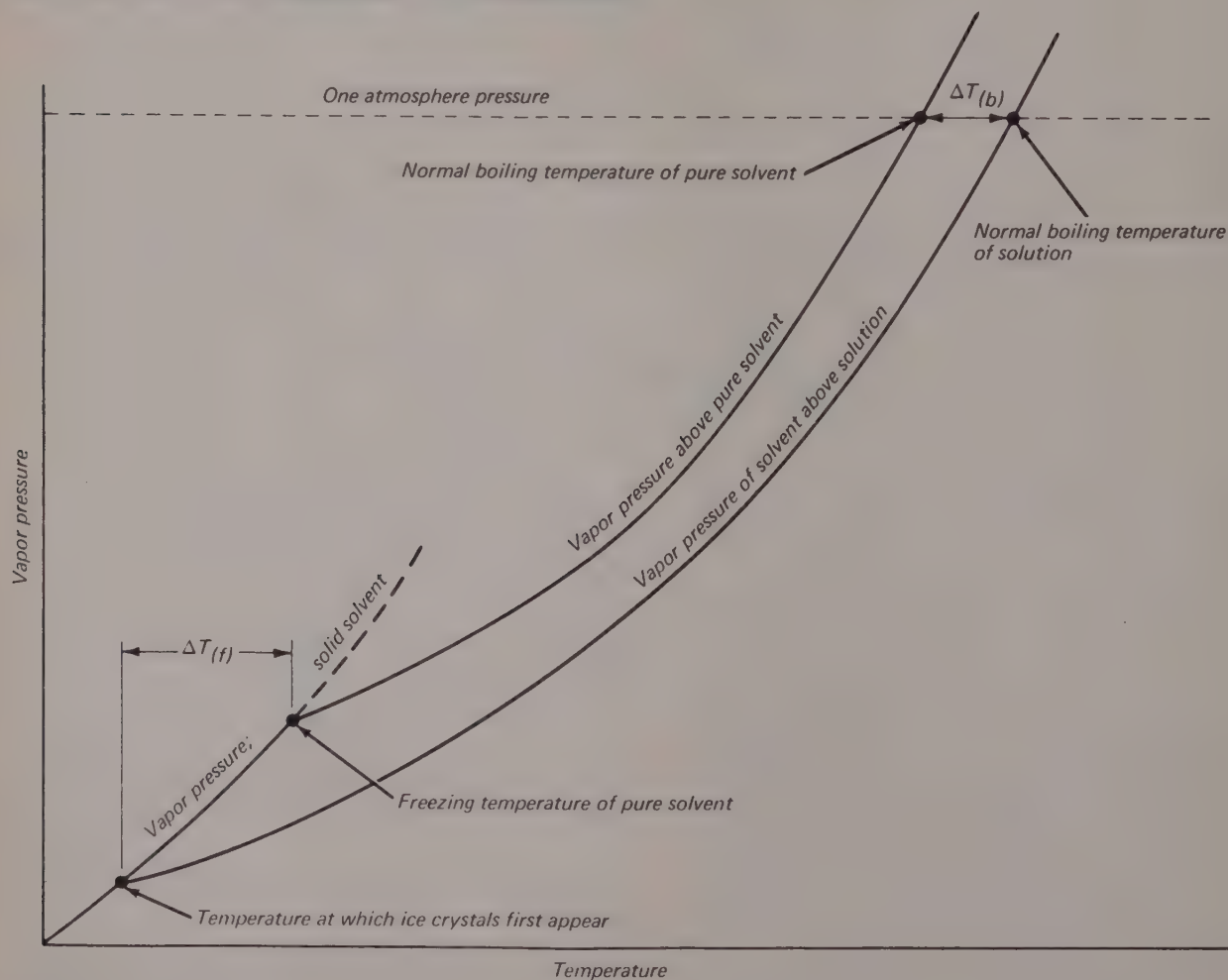


FIGURE 6-1

Liquid and solution vapor pressure versus temperature.

Raoult's Law can be expressed as

$$\frac{\text{Pressure solvent above solution}}{\text{Pressure pure solvent}} = \frac{\text{No. solvent molecules}}{\text{No. solvent molecules} + \text{No. solute molecules}}$$

or,

$$P = P_0 \times N_1$$

where

P = vapor pressure of solvent above solution ;

P_0 = vapor pressure of pure solvent ;

N_1 = mole fraction of solvent in solution as defined above.

We note in the Text that the solid phase separating from a fairly dilute aqueous solution of sugar is pure water and that the vapor phase above an aqueous solution of sugar in water is also pure water. These facts are used in our diagram: the solid-vapor equilibrium line is the same as that of pure solvent; and our solution will boil when the vapor pressure of the *solvent* above the solution is one atmosphere. The solution will freeze where the solid-vapor and liquid-vapor lines meet or at the point where both solution and solid have the same vapor pressure. If solution and solid did not have the same vapor pressure, the phase of higher vapor pressure would evaporate and condense on the phase of lower vapor pressure until both phases did have the same pressure or until one phase disappeared.

It is apparent from Figure 6-1 that the boiling temperature of the solution is raised by an amount ΔT_b and that its freezing temperature is lowered by an amount ΔT_f . Both changes result from vapor pressure changes and are thus related to the concentration of the solution. For the boiling temperature, the effect is direct and easily visualized, but for the freezing temperature, the relation to vapor pressure is less direct and demands a somewhat more detailed review of the equilibrium existing in a liquid-solid system.

Distillation

The process of distillation is one of the most widely used methods for separating components of solutions. We are now in a position to extrapolate our previous arguments and to consider the process of distillation. Suppose that we have

a mixture of two liquids, *A* and *B*, both of which are volatile. The volatility of each will be reduced by the presence of the other. The vapor pressure of *A* may be plotted as a function of the mole fraction of *A* present in the mixture. If *A* obeys Raoult's Law ($P = P_0 \times N_1$), the plot will be a straight line, as shown in Figure 6-2. The corresponding plot for the vapor pressure of *B* will be a line sloping in the other direction. The total pressure of the solution will be the sum of the two partial pressures, and is represented by the third line in Figure 6-2. To illustrate clearly and quantitatively the basis of a distillation process let us examine the composition of the vapor which is in equilibrium with a solution containing 0.8 mole fraction of *A* and 0.2 mole fraction of *B*. Our curves show that the vapor pressures are 30 mm for *B*, 70 mm for *A*, and 100 mm total. The mole fraction of *A* in the vapor is then

$$\frac{70}{30 + 70} = 0.70$$

The line labeled *vapor* shows the mole fraction composition of the vapor phase. It is obviously richer in *B*, the more volatile component, and poorer in *A*, the less volatile component. If this vapor is condensed, the liquid will be richer in *B* than was the original. Part of the recondensed liquid could then be vaporized. Again the vapor would be richer in *B*, and if this vapor were condensed, a liquid still richer in *B* would be obtained. Repetition of this process, known as isothermal distillation, can give a product whose composition approaches more closely at each step to that of pure *B*.

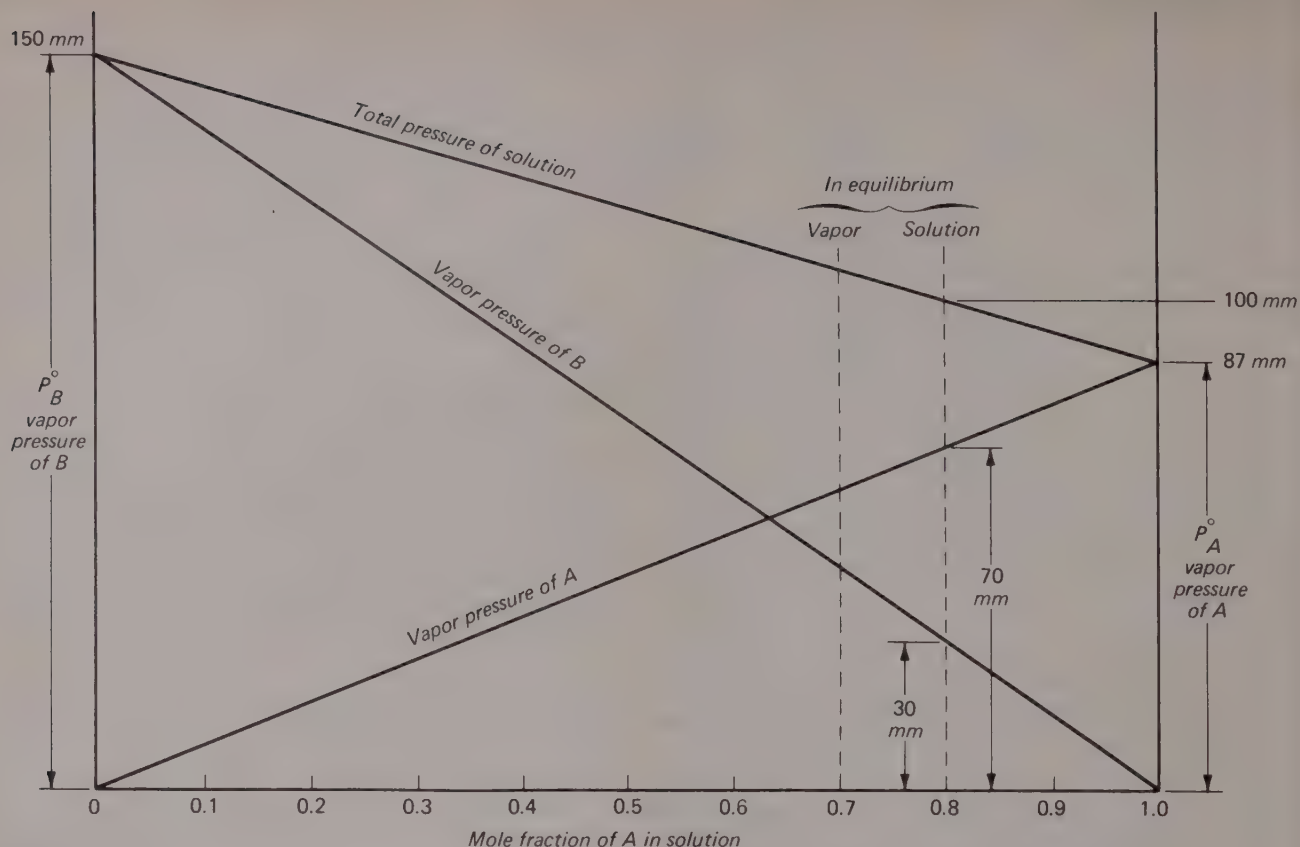


FIGURE 6-2

Vapor pressure of a solution of two liquids (hypothetical case).

Coulomb's Law

Coulomb studied the effects of charged bodies quantitatively in 1789. If one body has a charge q_1 and a second body has a charge q_2 , the force (whether attracting or repelling) varies directly with the product of the quantities q_1 and q_2 . The greater the product, q_1q_2 , the greater the force. The force also depends upon the distance between the charged particles; it decreases with the square of the distance between the charges.

A reasonable picture can be proposed to explain why the force varies inversely as the square of the distance. We can consider that a charged particle exerts its influence in all possible directions. The second particle can lie anywhere on the surface of an assumed sphere of radius r having the first particle at its center; the second particle "feels," or intercepts, only part of the influence of the first. If the distance r is doubled, the surface of the sphere is quadrupled (surface =

$4\pi r^2$). Then the second particle "feels" only one-fourth as much as before.

Students who have had physics may ask why the dielectric constant of the medium is not mentioned in the expression of Coulomb's Law. It is, of course, a part of the proportionality constant in the equation. Further discussion should be reserved for after class for those students who raise the question. Emphasize that we are interested only in Coulomb's Law in empty space.

It has been observed experimentally, of course, that the coulombic force depends upon the nature of the medium between the charged particles. The force between two charged objects may be lessened when a material is placed between them. The material seems to "insulate" the charges from each other. Since the dependence of force upon the charges and distance is unchanged, the entire effect of the change in medium is expressed as a change in the propor-

tionality constant. One way of doing this is in terms of the dimensionless constant ϵ , called the dielectric constant. It is the ratio of the force in a vacuum to that in the material. In a vacuum,

$$F = \frac{-k(\text{vac})q_1q_2}{r^2}$$

In a medium m ,

$$F = \frac{-k(\text{vac})q_1q_2}{\epsilon_m r^2}$$

where ϵ_m is the dielectric content of medium m .

The Role of the Solvent

The professional chemist must be concerned with the properties of many solvents. In high school chemistry, owing both to the limitation of time and to the complexity of treatment, you will examine only one solvent in detail—water. Recall that water possesses several properties unexpected for a compound of such small molar mass. If we assume the van der Waals forces in water to be of the magnitude of those that exist in hydrocarbons, then the boiling temperature of water is about what we would expect for a compound having a molar mass of 100 (C_7H_{16} , molar mass 100, b.t. = 98.4°C). If only forces of this nature existed, water would surely have a boiling temperature less than that of H_2S , -60.8°C . The high boiling temperature and other unusual properties of water (melting temperature, heat of melting, heat of vaporization) are related to the tendency of its molecules to clump together and form large molecular aggregates. This property is explained in terms of hydrogen bonding, which will be treated in Chapters 10 and 17.

In addition to forming hydrogen bonds, water has a dipole moment resulting from the O—H bonds, which form an angle of about 105° . Because of their dipole character, water molecules align themselves in a more or less regular manner when they form larger molecular aggregates in the liquid. This arrangement greatly enhances the effect of their dipole moment, giving water a high *dielectric constant*. This constant

is really part of the full equation for the attractive force between two charges. Its inclusion is often not apparent because the proportion given is for a vacuum having a dielectric constant equal to unity. Dielectric constant is found to enter the denominator of the equation; hence one can see that the larger the constant, the smaller the force of attraction between charged particles.

When substances are dissolved in water three processes may occur, according to the nature of the substance: (1) the molecules may simply separate and become hydrated (alcohol in water); (2) the ions may separate and become hydrated (NaCl in water); or (3) the molecules may form ions which become hydrated (HCl in water). Substances which simply dissolve probably do so according to a process by which their molecules form hydrogen bonds with water molecules. Salts separate into ions because, as mentioned above, the electrostatic attraction between the ions is overcome by the attraction to water. The reason that molecules of some substances dissociate in water to form ions is a bit more subtle. Background for understanding this will be given later in Chapters 16–17.

Solubility Equilibria

The Textbook lists several solubility rules in Table 6-2. You should encourage the student to make maximum use of these. It might prove interesting, however, to take an overview of solubility. The extent to which a solid substance will dissolve is governed by minimum energy and maximum randomness. For solids, randomness always favors dissolution because the solid is ordered and the solution is disordered. Insofar as energy is concerned, whether a substance will dissolve in water depends upon the energy the substance possesses as a solid and the energy it possesses when dispersed in water. We expect the state of lowest energy to be the preferred one. The solid state (not dissolved) will be favored by high interionic attraction, low hydration energy, and efficient packing in the crystal lattice. The magnitude of interionic attraction

will be greater with larger charge on the ion and smaller ionic size. Most solids containing covalent bonds have low solubility in water because the energy required to pull the molecules away from each other is greater than the energy released when the molecules become hydrated. Dissolution is favored by low interionic attraction in the solid and high hydration energy of the dissolved ions or molecules.

The Nature of Solution Processes

A detailed consideration of solubility phenomena should involve the analysis of two terms: the change in heat content, or ΔH for the process; and the change in entropy, or ΔS for the process. These are combined to give free energy, ΔG .

$$\Delta G = \Delta H - T\Delta S$$

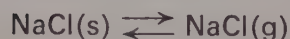
We can picture an ionic solid dissolving, and imagine breaking the process into separate energy terms, each of which represents the making or breaking of various bonds or the alteration of various intermolecular or interionic attractions. Then if we add up the energy terms associated with each of the separate steps, we can get ΔH for the process of solution.

Let us analyze ΔH for the process involved in dissolving a crystalline solid such as NaCl. We may consider a *number of hypothetical steps* involving energy terms, each of which can be pictured easily from our model. Such an analysis helps us to see which bonds or interactions are of significance for the process being considered, but it does not imply that solution proceeds by the steps used for the analysis. The net equation is:



where $\text{Na}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$ represent the ions in a water solution. The following steps may be conveniently assumed:

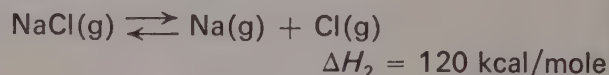
1. Vaporization of NaCl produces gaseous molecules of NaCl.



$$\Delta H_1 = 40 \text{ kcal/mole}$$

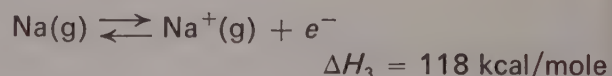
This is an endothermic process, the heat being the heat of sublimation.

2. Adding enough energy to break the bond produces neutral atoms:



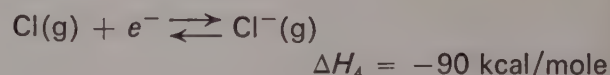
This is an endothermic process, the observed heat being the bond energy.

3. Ionization of the sodium atom is shown by the reaction



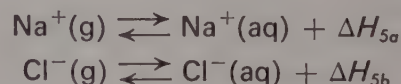
This reaction is endothermic, the observed heat being the ionization energy.

4. Ionization of the chlorine atom follows the reaction



This is the first exothermic step, and it releases about 90 kcal (less heat than step 3 absorbs).

5. Now let's dissolve these two ions in water.



Adding all of the heats, we must get ΔH for the overall process, which is usually only a few kcal (for NaCl it is -1 kcal/mole).

$$\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_{5a} + \Delta H_{5b} = \text{heat of solution}$$

$$\begin{aligned} (+40) + (+120) + (+118) + (-90) \\ + \Delta H_{5a} + \Delta H_{5b} = -1 \text{ kcal/mole} \end{aligned}$$

$$\Delta H_{5a} + \Delta H_{5b} = -180 \text{ kcal/mole}$$

We see that the sum of ΔH_{5a} and ΔH_{5b} is exothermic by almost 200 kcal. This is the result of two processes:

- (a) When a positive ion dissolves, it interacts with the negative ends of the water molecules.
- (b) When a negative ion dissolves, it interacts with the positive ends of the water molecules.

The heat change for the overall process involves the sum of the heat terms for each of the above five steps. Since the large energy needed to pull the positive and negative ions apart in step 1 must be provided by the interaction of positively and negatively charged ions with the charged ends of the solvent, it is clear why salts dissolve most readily in polar solvents (solvents having a positive and negative end). Nonpolar molecules do not interact strongly with the ions (as in step 5) to provide energy for the endothermic steps, thus the process becomes prohibitively endothermic.

To get an estimate of ΔS for the process from

our model is much more difficult and involves a statistical study of the disorder of the system. In general the second term ($-T\Delta S$) for a solution process is negative and may dominate *slightly* endothermic processes but *not* strongly endothermic ones.

For substances like paraffin and gasoline, in which nonpolar molecules are held together loosely, the ΔH (solution) is small, and the prime driving force is ($-T\Delta S$). The most direct explanation of $T\Delta S$ is that it measures the disorder in a system. If we go from an ordered system such as two components in separate bottles to a disordered system in which the two components are randomly mixed in a solution, the $T\Delta S$ value is positive, and ($-T\Delta S$), appearing in our equation for ΔG , is negative. This makes ΔG more negative; and our driving force for the process, greater.

Answers to Exercises and Problems

Exercise 6-1

What mass of AgNO_3 is needed to make 1 liter of 1 M solution?

Answer

1 liter of any 1 M solution requires 1 mole of solute. Molar mass of AgNO_3 is

$$107.8 + 14.0 + 3(16.00) = 169.8 \text{ or } 170 \text{ g.}$$

Therefore, 170 g AgNO_3 is needed to make 1 liter of 1 M solution.

Exercise 6-2

What mass of AgNO_3 is needed to make 100 ml of 2 M solution?

Answer

1 molar mass in 1 liter of solution gives 1 M

2 molar masses in 1 liter of solution give 2 M

0.2 molar mass in 0.1 liter of solution gives 2 M

(0.2 mole) (169.8 g AgNO_3 /mole)

$$= 33.9 \text{ or } 34 \text{ g } \text{AgNO}_3 \text{ required}$$

Exercise 6-3

You have 8.4 grams of solid sodium bicarbonate, NaHCO_3 . How many moles of solid is this? How much 1 M solution can be made with this amount of NaHCO_3 ?

Answer

Molar mass NaHCO_3

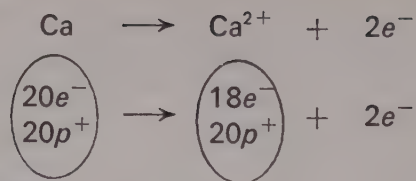
$$= 23.0 + 1.0 + 12.0 + 3(16.0) = 84.0 \text{ g}$$

$$\frac{8.4 \text{ g } \text{NaHCO}_3}{84 \text{ g } \text{NaHCO}_3/\text{mole}} = 0.10 \text{ mole}$$

We could make 0.10 liter of 1 M solution with this amount of solid.

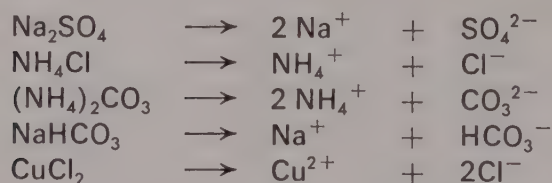
Exercise 6-4

A neutral calcium atom has 20 electrons and 20 protons. Show the formation of Ca^{2+} as an electron loss process.

Answer**Exercise 6-5**

The solids listed below dissolve readily in water to give solutions that conduct electricity. For each substance write an equation to represent what happens. The four ions (sulfate, ammonium, carbonate, and hydrogen carbonate) act as units in the same way nitrate ion does. What electric charges would each of these ions have?

Na_2SO_4	Sodium sulfate
NH_4Cl	Ammonium chloride
$(\text{NH}_4)_2\text{CO}_3$	Ammonium carbonate
NaHCO_3	Sodium hydrogen carbonate
CuCl_2	Cupric chloride

Answer**Problem 1**

List three heterogeneous materials.

Answer

Concrete
A piece of wood
A brick wall
A mosaic
A piece of candy with a soft center
Milk

Changing the "scale" at which observation is made can lead to interesting discussion. What appears heterogeneous close up may seem uniform from a distance. Homogenized milk can be used as an example; it appears uniform, but it actually consists of small drops of butter fat suspended in a solution.

Problem 2

List three homogeneous materials.

Answer

Gasoline or many other liquid solutions

Any pure compound

Honey

Glass

Problem 3

Which of the following statements about seawater is FALSE?

- It boils at a higher temperature than pure water.
- It melts at a lower temperature than pure water.
- The boiling temperature rises as the liquid boils away.
- The melting temperature falls as the liquid freezes.
- The density is the same as that of pure water.

Answer: (e).**Problem 4**

Early gold miners collected very fine gold dust from their sluice boxes by dissolving it in mercury. How do you think the gold was then separated from the mercury?

Answer

The mercury was distilled away by heating the mixture. The gold remained in the container.

Problem 5

Would ocean water in which ice has been formed and then removed be a better source of salt than untreated ocean water? Explain.

Answer

Yes. When the ice freezes from a solution, it is largely pure water. Little of the solute is enclosed. Thus, the solution remaining is richer in solute than the original solution.

Problem 6

How many grams of methanol, CH_3OH , must be added to 2.00 moles of H_2O to make a solution containing equal numbers of H_2O and CH_3OH molecules? How many molecules (of all kinds) does the resulting solution contain?

Answer

To obtain a solution containing equal numbers of H_2O and CH_3OH molecules, we must mix equal numbers of moles. To 2.00 moles of water we must add 2.00 moles of CH_3OH . The molar mass of CH_3OH is 32.0, so 64.0 g contain 2.00 moles.

The solution contains 4.00 moles, hence

$$(4.00) \times (6.0 \times 10^{23}) = 2.4 \times 10^{24} \text{ molecules}$$

Problem 7

How many grams of ammonium chloride, NH_4Cl , are present in 0.30 liter of a 0.40 M NH_4Cl solution?

Answer: 6.4 grams.

Answer

$$(0.30 \text{ liter})(0.40 \text{ mole/liter}) = 0.12 \text{ mole } \text{NH}_4\text{Cl}$$

$$(0.12 \text{ mole})(53.5 \text{ g/mole}) = 6.4 \text{ g } \text{NH}_4\text{Cl}$$

Problem 8

Write directions for preparing the following aqueous solutions:

- (a) 1.0 liter of 1.0 M lead nitrate, $\text{Pb}(\text{NO}_3)_2$, solution
- (b) 2.0 liters of 0.50 M ammonium chloride, NH_4Cl , solution
- (c) 0.50 liter of 2.0 M potassium chromate, K_2CrO_4 , solution

Answer

- (a) $(1.0 \text{ liter})(1.0 \text{ mole/liter}) = 1.0 \text{ mole } \text{Pb}(\text{NO}_3)_2$ needed. Therefore, dissolve 331 g of $\text{Pb}(\text{NO}_3)_2$ in sufficient water to make the final volume equal to 1.0 liter.
- (b) $(2.0 \text{ liters})(0.50 \text{ mole/liter}) = 1.0 \text{ mole } \text{NH}_4\text{Cl}$ needed. Therefore, dissolve 54 g of NH_4Cl in sufficient water to make the final volume equal to 2.0 liters.
- (c) $(0.50 \text{ liter})(2.0 \text{ moles/liter}) = 1.0 \text{ mole } \text{K}_2\text{CrO}_4$ needed. Therefore, dissolve 194 g of K_2CrO_4 in sufficient water to make the final volume equal to 0.50 liter.

Problem 9

How many liters of 0.250 M K_2CrO_4 solution contain 38.8 grams of K_2CrO_4 ?

Answer

$$38.8 \text{ g} \times \frac{1}{194 \text{ g/mole}} = 0.200 \text{ mole } \text{K}_2\text{CrO}_4$$

$$0.200 \text{ mole} \times \frac{1 \text{ liter}}{0.250 \text{ mole}} = 0.800 \text{ liter}$$

Problem 10

Which has the greater solubility in water:

- (a) pepper or salt
- (b) CO_2 or N_2
- (c) oil or molasses
- (d) limestone or granite

Answer

- (a) salt

(b) CO_2

(c) molasses

(d) limestone; recall formations in limestone caves

Problem 11

One liter of saturated calcium carbonate solution contains 0.0153 gram at 25°C. What is the solubility of CaCO_3 in moles/liter?

Answer

$$\text{solubility} = \left(\frac{0.0153 \text{ g } \text{CaCO}_3/\text{liter}}{100.1 \text{ g } \text{CaCO}_3/\text{mole}} \right)$$

$$= 0.000153 \text{ or } 1.53 \times 10^{-4} \text{ mole/liter}$$

Problem 12

Name three chemicals that readily dissolve in water. Name three that scarcely dissolve at all.

Answer

NaCl (salt), alcohol, sugar, and NaHCO_3 dissolve readily.

Gold, silver, SiO_2 (glass, sand), gasoline, oil, and carbon scarcely dissolve.

Problem 13

List three properties of a solution you would expect to vary as the concentration of the solute varies.

Answer

- (a) Density
- (b) Boiling temperature
- (c) Viscosity
- (d) Color in some cases
- (e) Freezing temperature
- (f) Chemical action

Problem 14

Give two forces other than electric that are felt at a distance.

Answer

Gravitational
Magnetic

Problem 15

Why do two electrically neutral objects with mass attract each other?

Answer

The attraction of objects with mass is a fundamental property of matter. There is no model to explain this. The answer "Because of gravity" of course explains nothing; it is just the name of the mystery.

Problem 16

Why do scientists claim there are only two kinds of electric charge?

Answer

No others have been found.

Problem 17

The following 6 measurements were obtained during a Millikan oil-drop experiment. They represent the electric charge on the drop.

4.83×10^{-19} coulomb	6.44×10^{-19} coulomb
3.24	4.80
9.62	1.62

- Might one of these values correspond to the unit electric charge? Which one? Why?
- Can you think of an argument to rule out the value 0.81×10^{-19} coulomb as the unit electric charge?

Answer

- One might. It would have to be the smallest one, 1.62×10^{-19} coulomb. To test, divide it into each other value, getting 2.98, 2.00, 5.94, 3.99, 2.96. Allowing for experimental error, these values are near enough to the integers 3, 2, 6, 4, 3.
- The value 0.81×10^{-19} coulomb for the unit electric charge should lead to observed values of

$$(0.81, 1.62, 2.43, 3.24, 4.05, 4.86, 5.67) \times 10^{-19}$$

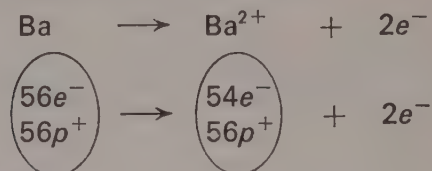
The set given includes none for 2.43, 4.05, or 5.67×10^{-19} (and neither do the larger collections of data Millikan obtained). Thus, 0.81×10^{-19} is not acceptable as the unit charge.

Problem 18

A neutral atom of barium has 56 electrons. Barium forms a $2+$ ion. How many protons does a barium ion have? How many electrons in the $2+$ ion? Show the formation of the ion as an electron loss process.

Answer

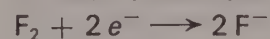
A neutral Ba atom has 56 protons. The $2+$ ion has 54 electrons and 56 protons.

**Problem 19**

A neutral fluorine atom has 9 protons. Fluorine, F, forms an ion with $1-$ charge. How many electrons does a fluoride ion, F^{-} , have? Starting with F_2 , show the formation of F^{-} as an electron gain process. Check to see that charge is balanced.

Answer

F^{-} has 10 electrons.

**Problem 20**

What would you expect the empirical formula for barium fluoride to be?

Answer

BaF_2 since it takes two negative charges (2F^{-}) to combine with the two positive charges (Ba^{2+}) and achieve electric neutrality.

Problem 21

Each of the following ionic solids dissolves in water to form conducting solutions. Write equations for each reaction.

- potassium chloride, KCl
- sodium nitrate, NaNO_3
- calcium bromide, CaBr_2
- lithium iodide, LiI

Answer

- $\text{KCl} \longrightarrow \text{K}^{+} + \text{Cl}^{-}$
- $\text{NaNO}_3 \longrightarrow \text{Na}^{+} + \text{NO}_3^{-}$
- $\text{CaBr}_2 \longrightarrow \text{Ca}^{2+} + 2\text{Br}^{-}$
- $\text{LiI} \longrightarrow \text{Li}^{+} + \text{I}^{-}$

Problem 22

A chloride of iron called ferric chloride, FeCl_3 , dissolves in water to form a conducting solution containing ferric ions, Fe^{3+} , and chloride ions, Cl^{-} .

- Write the equation for this reaction.
- If 0.10 mole of FeCl_3 is dissolved in 1.0 liter of water, what is the concentration of ferric ion and of chloride ion?

Answer: Concentration of $\text{Fe}^{3+} = 0.10\text{ M}$.
Concentration of $\text{Cl}^{-} = 0.30\text{ M}$.

Answer

- (a) $\text{FeCl}_3 \longrightarrow \text{Fe}^{3+} + 3 \text{Cl}^-$
 (b) 0.10 mole of FeCl_3 gives 0.10 mole of Fe^{3+} ions and 0.30 mole of Cl^- ions. Hence, the concentrations are:

$$\text{Fe}^{3+} = \frac{0.10 \text{ mole}}{1.0 \text{ liter}} = 0.10 M$$

$$\text{Cl}^- = \frac{0.30 \text{ mole}}{1.0 \text{ liter}} = 0.30 M$$

Problem 23

The salt ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, dissolves in water to form a conducting solution containing ammonium ions, NH_4^+ , and sulfate ions, SO_4^{2-} .

- (a) Write the balanced equation for the reaction when this ionic solid dissolves in water.
 (b) Verify the conservation of charge by comparing the charge of the reactant to the sum of the charges of the products.
 (c) Suppose 1.32 grams of ammonium sulfate is dissolved in 0.500 liter of water. Calculate the concentrations of $\text{NH}_4^+(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$.

Answer

- (a) $(\text{NH}_4)_2\text{SO}_4 \longrightarrow 2 \text{NH}_4^+ + \text{SO}_4^{2-}$
 (b) reactant products
 0 charge $2(1+) + (2-)$
 $= (2+) + (2-) = 0$

- (c) The number of moles in 1.32 g of $(\text{NH}_4)_2\text{SO}_4$

$$\text{is } \frac{1.32 \text{ g}}{132 \text{ g/mole}} = 0.0100 \text{ mole}$$

$$\text{moles } \text{NH}_4^+ = 2(0.0100) = 0.0200 \text{ mole}$$

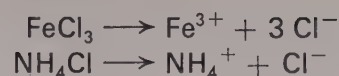
$$\text{moles } \text{SO}_4^{2-} = 0.0100 \text{ mole}$$

$$\text{concentration } \text{NH}_4^+ = \frac{0.0200 \text{ mole}}{0.500 \text{ liter}} = 0.0400 M$$

$$\text{concentration } \text{SO}_4^{2-} = \frac{0.0100 \text{ mole}}{0.500 \text{ liter}} = 0.0200 M$$

Problem 24

For 1.00 liter of solution made from 0.100 mole of ferric chloride, FeCl_3 , and 0.100 mole of ammonium chloride, NH_4Cl , calculate the molar concentrations of the three ions Fe^{3+} , NH_4^+ , and Cl^- .

Answer

From 0.100 mole of FeCl_3 , we obtain 0.100 mole of Fe^{3+} ions and 0.300 mole of Cl^- ions. From 0.100 mole of NH_4Cl , we obtain 0.100 mole of NH_4^+ ions and 0.100 mole of Cl^- ions. Hence the concentrations are

$$\text{Fe}^{3+} = \frac{0.100 \text{ mole}}{1.00 \text{ liter}} = 0.100 M$$

$$\text{NH}_4^+ = \frac{0.100 \text{ mole}}{1.00 \text{ liter}} = 0.100 M$$

$$\text{Cl}^- = \frac{0.300 + 0.100 \text{ mole}}{1.00 \text{ liter}} = 0.400 M$$

Problem 25

Assume the following compounds dissolve in water to form separate, mobile ions in solution. Write the formulas and the names for the ions that can be expected.

- | | |
|------------------------------|------------------------------|
| (a) HI | (d) $\text{Ba}(\text{OH})_2$ |
| (b) CaCl_2 | (e) KNO_3 |
| (c) Na_2CO_3 | (f) NH_4Cl |

Answer

- (a) H^+ , hydrogen ion; I^- , iodide ion.
 (b) Ca^{2+} , calcium ion; Cl^- , chloride ion.
 (c) Na^+ , sodium ion; CO_3^{2-} , carbonate ion.
 (d) Ba^{2+} , barium ion; OH^- , hydroxide ion.
 (e) K^+ , potassium ion; NO_3^- , nitrate ion.
 (f) NH_4^+ , ammonium ion; Cl^- , chloride ion.

Problem 26

Write the equation for the reaction that occurs when each of these electrolytes is dissolved in water.

- (a) lithium hydroxide (solid)
 (b) nitric acid (liquid)
 (c) potassium sulfate (solid)
 (d) sodium nitrate (solid)
 (e) ammonium iodide (solid)
 (f) potassium carbonate (solid)

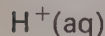
Answer

- (a) $\text{LiOH} \longrightarrow \text{Li}^+ + \text{OH}^-$
 (b) $\text{HNO}_3 \longrightarrow \text{H}^+ + \text{NO}_3^-$
 (c) $\text{K}_2\text{SO}_4 \longrightarrow 2 \text{K}^+ + \text{SO}_4^{2-}$
 (d) $\text{NaNO}_3 \longrightarrow \text{Na}^+ + \text{NO}_3^-$
 (e) $\text{NH}_4\text{I} \longrightarrow \text{NH}_4^+ + \text{I}^-$
 (f) $\text{K}_2\text{CO}_3 \longrightarrow 2 \text{K}^+ + \text{CO}_3^{2-}$

Problem 27

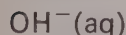
What ion will all the acids listed on page 95 form?

Answer

**Problem 28**

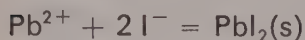
What ion will all the bases listed on page 95 form?

Answer

**Problem 29**

In Experiment 16 you mixed lead nitrate and sodium iodide solutions. Write an equation for the reaction that occurred. Show only the predominant species.

Answer

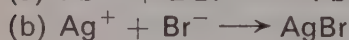
**Problem 30**

Write equations for the reactions between aqueous bromide ions and:

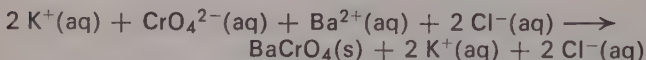
- (a) aqueous lead ions
- (b) aqueous silver ions

Use Table 6-2 to help you decide how to write these equations.

Answer

**Problem 31**

When solutions of barium chloride, BaCl_2 , and potassium chromate, K_2CrO_4 , are mixed, the following reaction occurs:



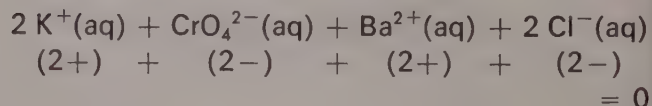
- (a) Show how charge is conserved.
- (b) Rewrite the equation showing predominant species only. Is charge conserved when the equation is written this way?
- (c) Suppose 1.00 liter of 0.500 *M* BaCl_2 is mixed with 1.00 liter of 0.200 *M* K_2CrO_4 . Assume that BaCrO_4 has negligible solubility. Calculate the concentrations of all ionic species present when precipitation is complete.

Answer: Concentration $\text{K}^+ = 0.200 \text{ M}$
 Concentration $\text{Cl}^- = 0.500 \text{ M}$
 Concentration $\text{CrO}_4^{2-} = \text{negligible}$
 Concentration $\text{Ba}^{2+} = 0.150 \text{ M}$

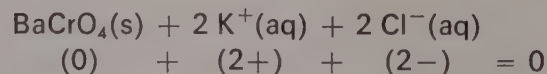
Answer

Emphasize net ionic equations and balance of charge.

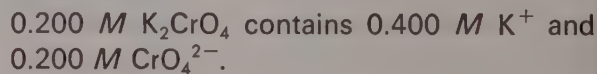
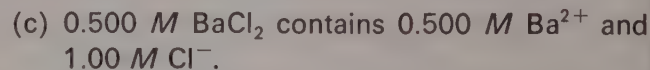
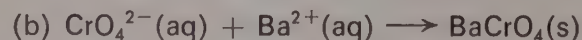
- (a) The sum of the electric charges among the reactants is:



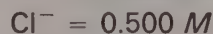
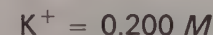
The sum of the electric charges among the products is:



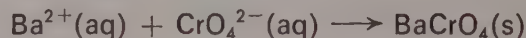
Summing these charges, we find that since $0 = 0$, charge has been conserved.



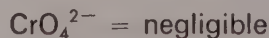
When the two solutions are mixed, the volume is doubled, so the concentrations of Cl^- and K^+ are halved.



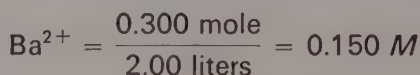
In addition, the reaction



will occur as long as both Ba^{2+} and CrO_4^{2-} remain (assuming negligible solubility of BaCrO_4). Since there is an excess of Ba^{2+} , virtually all of the CrO_4^{2-} will be consumed.



The solution originally contained 0.500 mole of Ba^{2+} but 0.200 mole are precipitated by the CrO_4^{2-} . The remaining 0.300 mole of Ba^{2+} is dissolved in 2.00 liters, hence

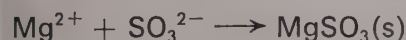


Problem 32

Predict what would happen if equal volumes of 0.2 *M* Na₂SO₃ and 0.2 *M* MgSO₄ were mixed. If a reaction takes place, write the net ionic equation.

Answer

A precipitate of MgSO₃ would form.

**Problem 33**

Using Table 6-2 make a statement about the solubilities of the compounds containing the following ions.

Anion	Cations
(a) carbonate, CO ₃ ²⁻	alkali ions, (Li ⁺ , Na ⁺ , K ⁺ , Rb ⁺ , Cs ⁺)
(b) carbonate, CO ₃ ²⁻	alkaline earth ions, (Be ²⁺ , Mg ²⁺ , Ca ²⁺ , Sr ²⁺ , Ba ²⁺)
(c) sulfide, S ²⁻	alkaline earth ions, (Be ²⁺ , Mg ²⁺ , Ca ²⁺ , Sr ²⁺ , Ba ²⁺)

Answer

- (a) All alkali carbonates are soluble.
- (b) All alkaline earth carbonates have low solubilities.
- (c) All alkaline earth sulfides are soluble.

Problem 34

Write an empirical formula for each of the following compounds and indicate which have low solubilities.

- (a) silver sulfide
- (b) potassium sulfide
- (c) ammonium sulfide
- (d) nickel sulfide
- (e) ferrous sulfide
- (f) ferric sulfide

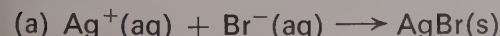
Answer

- (a) Ag₂S (low)
- (b) K₂S
- (c) (NH₄)₂S
- (d) NiS (low)
- (e) FeS (low)
- (f) Fe₂S₃ (low)

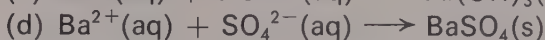
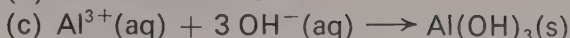
Problem 35

Write a net ionic equation for any reaction that will occur upon mixing equal volumes of 0.2 *M* solutions of the following pairs of compounds.

- (a) silver nitrate and ammonium bromide
- (b) SrBr₂ and NaNO₃
- (c) sodium hydroxide and aluminum chloride
- (d) barium chloride and sodium sulfate

**Answer**

(b) No solids will form.

**Problem 36**

What ions could be present in a solution if samples of it gave:

- (a) A precipitate when either Cl⁻(aq) or SO₄²⁻(aq) is added?
- (b) A precipitate when Cl⁻(aq) is added but none when SO₄²⁻(aq) is added?
- (c) A precipitate when SO₄²⁻(aq) is added but none when Cl⁻(aq) is added?

Answer

- (a) Pb²⁺(aq) must be present.
- (b) One or more of Cu⁺(aq), Ag⁺(aq), and Hg₂²⁺ must be present.
- (c) One or more of Ca²⁺(aq), Sr²⁺(aq), and Ba²⁺(aq) must be present.

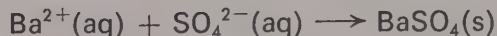
Problem 37

Use Table 6-2 to decide which of the following soluble substances would permit a separation of aqueous magnesium from barium ions. For those that are effective, write the equation for the reaction that occurs.

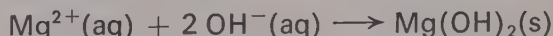
- (a) ammonium carbonate
- (b) sodium bromide
- (c) potassium sulfate
- (d) sodium hydroxide

Answer

- (a) No separation; both cations precipitate.
- (b) No separation; neither cation precipitates.
- (c) Separation possible.



- (d) Separation possible.

**Problem 38**

Some 2 *M* NaBr solution is added to a sample which is 0.1 *M* in each of the following ions, Ag⁺, Cu⁺, Fe²⁺, and Ca²⁺. Precipitate *A* forms and is filtered out. A sulfide solution is added to the filtrate and black precipitate *B* forms. This precipitate is removed by filtration and 2 *M* sodium carbonate solution is added, giving precipitate *C*. What is the composition of *A*, *B*, and *C*?

Answer

A is a mixture of AgBr and CuBr.

B is FeS.

C is CaCO₃.

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

- Positive ions are formed from neutral atoms by the loss of
 - protons
 - water
 - energy
 - electrons
 - none of these

Answer: (d).

- Give the formula of two metal ions that have the same number of electrons as Na^+ .

Answer: Mg^{2+} , Al^{3+} .

- Which of the following pairs of ions would be expected to form precipitates when equal volumes of 0.2 M solutions are mixed? Write formulas for the precipitates formed.

- Na^+ , SO_4^{2-}
- Ba^{2+} , CO_3^{2-}
- NH_4^+ , CO_3^{2-}
- Fe^{3+} , OH^-
- Pb^{2+} , Cl^-
- Na^+ , S^{2-}
- Ca^{2+} , PO_4^{3-}

Answer

- BaCO_3 .
- $\text{Fe}(\text{OH})_3$.
- PbCl_2 .
- $\text{Ca}_3(\text{PO}_4)_2$.

Given 2×10^{-3} M solutions of $\text{Pb}(\text{NO}_3)_2$ and Na_2SO_4 , determine answers to the next two questions.

- What ions will be present in each of the solutions? And in what concentrations?

Answer

Pb^{2+} , NO_3^- in the first, and Na^+ and SO_4^{2-} in the second. The concentrations are:

$$\text{Pb}^{2+} = 2 \times 10^{-3} \text{ mole/liter}$$

$$\text{NO}_3^- = 4 \times 10^{-3} \text{ mole/liter}$$

$$\text{Na}^+ = 4 \times 10^{-3} \text{ mole/liter}$$

$$\text{SO}_4^{2-} = 2 \times 10^{-3} \text{ mole/liter}$$

- Which ions are most likely to form a precipitate if the solutions are mixed?

Answer: Pb^{2+} and SO_4^{2-} .

- Which of the following would be expected to form ionic solutions in water?

- CO_2
- CCl_4
- C
- O_2
- NaI

Answer: (e).

- The compound HCN gives CN^- (cyanide ion) when dissolved in water. Given the clue that CN^- behaves somewhat as halide ions do, write formulas for the following compounds, and indicate those you would expect to have low solubility in water:

- ammonium cyanide,
- barium cyanide,
- silver cyanide.

Answer

- NH_4CN ; (b) $\text{Ba}(\text{CN})_2$; (c) AgCN , for which a low solubility is expected.

- Suppose you wish to separate Ba^{2+} from Co^{2+} . Which of these reagents could be successfully used: NaCl , Na_2CO_3 , NaOH ?

Answer

NaOH , since $\text{Co}(\text{OH})_2$ precipitates, whereas $\text{Ba}(\text{OH})_2$ does not.

Na_2CO_3 forms solids with both.

NaCl forms a solid with neither.

- Suggest why you would expect MgCl_2 to have a structure different from NaCl .

Answer

The empirical formula for MgCl_2 contains two chlorine atoms for each metal atom instead of one-to-one as there is in NaCl . Therefore, placing a Mg^{2+} ion where each Na^+ occurs in the NaCl lattice would give unbalanced charge. There must be only half that many cations but the same number of negative ions. Thus, a different structure might be expected.

10. Specify which of the following ions are monatomic or polyatomic and identify cations and anions.

Ti^+ , TeCl_6^{2-} , Te^{2-} , ReO_3^{2-} , $(\text{CH}_3)_4\text{N}^+$, N_3^- , $\text{Hg}_3\text{Cl}_3\text{O}^+$, ZrF_7^{3-} , U^{4+} , $\text{N}_2\text{H}_6^{2+}$

Answer

	Cation	Anion
Monatomic	Ti^+ , U^{4+}	Te^{2-}
Polyatomic	$(\text{CH}_3)_4\text{N}^+$	TeCl_6^{2-}
	$\text{Hg}_3\text{Cl}_3\text{O}^+$	ReO_3^{2-}
	$\text{N}_2\text{H}_6^{2+}$	N_3^- , ZrF_7^{3-}

11. What mass of NaOH(s) is needed to make 200 ml of 0.5 M solution?

Answer

Molar mass $\text{NaOH} = 23 + 16 + 1 = 40 \text{ g}$

$$\left(\frac{40 \text{ g NaOH}}{\text{mole}}\right) \left(\frac{0.5 \text{ mole}}{\text{liter}}\right) \left(\frac{200 \text{ ml}}{1000 \text{ ml/liter}}\right) = 4 \text{ g NaOH needed}$$

The following data are used in questions 12–14.

Sufficient Na_2S is dissolved in water to form a 2.0 M solution.

12. What is the concentration of each ion?

Answer

S^{2-} is 2.0 M

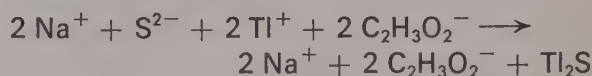
Na^+ is 4.0 M

13. What would you expect might happen if a 0.50 M solution of thallium acetate ($\text{TlC}_2\text{H}_3\text{O}_2$) is added to the sulfide solution?

Answer

The possible new combinations of ions are $\text{Na}^+\text{C}_2\text{H}_3\text{O}_2^-$ and $\text{Tl}_2^+\text{S}^{2-}$. Table 6-2 shows all acetates soluble and all sulfides not listed only slightly soluble. Therefore, a precipitate of Tl_2S might form. This salt has a solubility in water of 0.22 g/mole.

14. How much 0.5 M $\text{TlC}_2\text{H}_3\text{O}_2$ solution would be required to react with 20 ml of the Na_2S solution? Assume complete reaction.

Answer

$$\begin{aligned} &\left(\frac{20 \text{ ml}}{1000 \text{ ml/liter}}\right) \left(\frac{2 \text{ moles Na}_2\text{S}}{\text{liter}}\right) \\ &\quad \times \left(\frac{2 \text{ moles TIC}_2\text{H}_3\text{O}_2}{\text{mole Na}_2\text{S}}\right) \left(\frac{\text{liter}}{0.50 \text{ mole}}\right) \\ &= 0.16 \text{ liter TIC}_2\text{H}_3\text{O}_2 \text{ solution needed.} \end{aligned}$$

Order Among Atoms



Intent and Approach

Chapter 7 is an introduction to atomic structure and the Periodic Table. As the course advances, Chapters 8, 9, and 19 will add much more information about the table and treat it in depth. This chapter is confined to a study of experimental facts; trends in these facts are pointed out, but the effort to explain them and correlate them with structural theory is just barely started.

The details of periodic properties are given by demonstration. Then the table is discussed as an expression of "regularity." This approach convinces the students of the need for some sort of system for organizing information. The Periodic Table does this for a tremendous number of

chemical facts. The chemical inertness of the noble gases is used as a basis for organizing the regularities that occur in elements and, later, in compounds.

In this chapter the student will be exposed to many concepts and chemical facts. You must exercise care in order that neither you nor the student will feel buried by the flood. At this stage, center the student's attention on the chemistry which most pointedly displays the family relationships and periodicity. Remember that several later chapters will also deal with the Periodic Table.

Outline

The introduction indicates some historical facts: the recognition of metals and nonmetals and the occurrence of oxides of different formulas.

Development of the periodic concept starts (7-1) by an arrangement of the elements according to molar mass of the elements.

The noble gases are recognized as unusual

and used to suggest another ordering which yields groups of elements with similar properties. These groups are studied in greater detail: noble gases (7-2), alkali metals (7-3), and halogens (7-4).

A review terminates the chapter (7-5).

New Concepts

1. The periodic arrangement of elements emerges as a regularity.
2. The noble gases are chemically distinctive because they have relatively little chemical activity.
3. Ionization energy.

SCHEDULE AND RELATED MATERIAL

Suggested Time : 5 days

Text Section	Topic and Other Work	Exercises	Problems		
			Easy	Medium	Hard
7-1	The Periodic Table <i>Film: "Chemical Families"</i> fits well here		1	13	12, 15
7-2	The Noble Gases		3	2	
7-3	The Alkali Elements	1, 2		5	
7-4	The Halogens	3	8	6, 7, 11	14
7-5	Review <i>Note:</i> Expt. 19. Introduction to Qualitative Analysis, and Expt. 20. Qualitative Analysis—Relative Solubilities can fit anytime during this chapter. Perhaps slightly better after Section 7-2 is done.			4, 9, 10	

Development

Introduction

This chapter should be introduced by emphasizing the tremendous variety exhibited by the elements. One form of the variety lies in the range of melting temperatures, from about 14°K to above 1000°K. Such ranges are represented by the specific elements studied in this chapter. Another varying property is chemical reactivity. The elements considered in this chapter also illustrate a great range of this property.

There are about 100 elements, most of them capable of reaction, and there are about 100,000 *inorganic* compounds known. To remember several dozen facts about even a fraction of these is impossible. System and order must be discovered and used.

To develop this idea you might exhibit quite a sizeable number of elements and compounds from the stock room. Make the exhibit haphazard, so that no particular order is evident, and suggest to students what a job it would be for them if you started ticking off the properties of each element and saying that they were responsible for learning them all.

If you use elements only, then you can start a lively discussion by asking the students to group the materials. You may get a metal-nonmetal classification, a ranking by color, density, or hardness, or some other property. This exercise allows you to emphasize that the table permits the correlation of many experimental facts. Later in the semester we will be involved in explaining some of these properties.

Film, CHEMICAL FAMILIES,

fits here; see p. 122 for details.

7-1 The Periodic Table

Let the student understand that the Periodic Table is a regularity, discovered in the same way the lost child found "wooden objects burn." We have not presented the early trials—the triads and octaves—but you can mention them as part of the long process leading to the table. There has been continued development as new elements were made in the various high energy accelerators. A great deal of interest in their properties grew from the desire to see whether these elements resembled others in the rows immediately above them. Chapter 21 will contain further discussion of those man-made elements.

As to this section, itself, we use a much simplified version of what Mendeleev, himself, did. An important idea is to emphasize that facts (many more than we show) such as those in Table 7-4 were available to all chemists in the 1860's and 1870's. Organization was what was needed, plus some courage to say there must be other elements to fill certain places so the substances with similar properties will fall together.

Note that we have introduced atomic number but *without* identifying it. The student does not yet know about the nuclear atom and the neutron. They come in Chapter 8. At this stage, just let atomic number be "numerical order" as in Table 7-4.

Some properties are listed to show that hydrogen is unique. It should be included in neither the alkali nor the halogen group, because reliable predictions cannot be made from either grouping. This conclusion should cause no disturbance. Hydrogen doesn't *have* to fit into one of the families. The Periodic Table only states what regularities *do* exist among the elements. We must let experimental facts tell us what hydrogen "should" do. Additional evidence on this point is given later.

7-2 The Noble Gases

Take up the noble gases first. This is not the historical order of development, but it provides a key group to start with and gives a good point of departure for the brief account of electron arrangement given here.

In discussing the noble gases, emphasize the fact that properties of a group are being considered rather than properties of a single element. A group is shown as a column in the form of Periodic Table that we use.

The noble gases, having almost no chemistry, being colorless gases, and also not being readily available in high school laboratories, are a little hard to put before the student in a live demonstration. However, neon signs are familiar to all; some incandescent bulbs contain argon; and a variety of gas discharge tubes are often a part of a school's complement of physics equipment. You may choose to utilize these facts to convey the reality of the noble gases to your students.

Since the noble gases have almost no chemistry, the only properties to be mentioned are physical properties. The Textbook, however, covers these properties adequately, and no classroom discussion should be needed. Merely point out that the physical properties of the noble gases do not identify the noble gases as a group. The real uniqueness of the noble gases is their slight chemical reactivity.

The recent discovery of the first compounds of noble gases by Neil Bartlett [see H. H. Classen, *The Noble Gases*, D. C. Heath and Co., Boston, 1966 (paperback)] can be used to illustrate several points. First, it is a beautiful example of the way in which new experimental discoveries can alter a well-established theory. Second, there are still exciting things to be found—some of them relatively simple. Third, some new ideas of bonding will probably result. Even so, the new results do not vitiate the remarks in the Textbook. The noble gases *are* quite inert and do act as a unifying group for the Periodic Table.

Bartlett and others found that Xe and F₂ react at about 400°C to give XeF₄ (and, after photolysis, XeF₂), a colorless solid melting near 90°C.

It crystallizes in small cubes and looks like NaCl. Infrared and X-ray results show that it has a square planar, not a tetrahedral, structure. Radon forms similar compounds. Note that reactions with fluorine are to be undertaken only by those with some knowledge of the dangers. These new compounds are not suitable for study by beginning students.

Ionization energy is introduced in this section. This is an important property which provides experimental clues to both atomic structure and periodic chemical behavior. Make sure the student knows it. The film "Ionization Energy" might be used here or in the next chapter. See p. 153.

Expt. 19, INTRODUCTION TO QUALITATIVE ANALYSIS,

**Expt. 20, QUALITATIVE ANALYSIS—
RELATIVE SOLUBILITIES,**

can fit here or later in this chapter. See p. 104 and p. 106 in the Laboratory Guide.

7-3 The Alkali Elements

Again, emphasize to the student that he is studying a group of elements, and thus systematizing his accumulating knowledge of chemistry. This group of elements has one more electron than the nearest noble gas. These elements usually react by losing one electron to form positive ions. Point out their characteristics as metals, and then concentrate on the properties listed in Table 7-8 of the Textbook.

To answer the question of the opposite trends for melting temperature in alkali metals as compared with noble gases, suggest a difference in "bonding," and postpone giving a specific answer until Chapter 17. Very briefly, the answer follows these lines. The noble gas atoms of higher atomic number have more electrons and are larger. These larger atoms develop greater attraction and have higher melting temperatures. The alkali metal atoms also become larger and have more electrons as atomic number goes up. But the im-

portant number of valence electrons (one in this case) does not increase; the bonding strength does decrease, however, because other factors (atomic size) change.

Unlike the noble gases, the alkali metals exhibit a very observable chemistry. Sodium may be used as representative in a demonstration, though it surely won't be needed if the film "Chemical Families" is shown.

1. Cut two small pieces of sodium metal (smaller than a pea) such that clean surfaces are exposed. Place one piece in a bottle full of air or oxygen gas. Drop the second piece into a bottle of *dry* chlorine gas and let it stand. Observe the rate at which the white reaction products form.
2. Cut a third small piece of sodium metal (less than half the size of a pea). Work behind a glass plate for protection against spattering. Drop the sodium in pure water. Observe the rate of the reaction.

The reaction of sodium and chlorine is described in *Tested Demonstrations* (p. 58). See p. 122.

Go on to discuss the reaction of the alkali metals with chlorine and water, both of which are demonstrated in the film "Chemical Families."

7-4 The Halogens

Point out that a neutral atom for any element in this group is just one short of having the electron number of the nearest noble gas. It would be perfectly natural to expect these elements to enter reactions that would lead to the acquisition of electrons. In fact, the reaction of sodium and chlorine cited for the alkalies already says as much.

As do the alkali metals, the halogens show definite chemical reactivity. You may wish to demonstrate the production of Cl_2 , Br_2 , and I_2 and give some examples of their reactions to supplement the chemistry shown in the film "Chemical Families." *Do not use potassium*—it detonates with Br_2 and I_2 .

All the halogens attract electrons, and, in water solution, their tendency to form ions decreases from fluorine to iodine. Later (Chapter 19) you

can give some of the details of the postulated processes involved.

Electrons can be shared between atoms of different elements, forming relatively stable compounds. Hydrogen halides are illustrative of this. As dry gases, they are mostly covalent molecules. When put in water, they react with water, giving ions.

7-5 Review

The Textbook very briefly describes some of the history of the thinking that gave rise to the table. This is all the history that is needed.

Anyone particularly interested can be directed to Mendeleev's original paper (in English) in the *World of Mathematics*, Vol. II, pp. 913–918; Editor, J. R. Newman, Simon and Schuster, 1956. The paper following has an account of Mendeleev's life by B. Jaffe.

To summarize the chapter, try reviewing the student's acquaintance with the elements. Emphasize to the student that he can now claim an ordered knowledge about the properties of twenty elements and some of their compounds. Further, this ordered knowledge forms the basis for some fairly good guesses about the properties of other elements and their compounds.

Supplementary Material

Books

H. N. Alyea and F. B. Dutton, TESTED DEMONSTRATIONS IN CHEMISTRY, Journal of Chemical Education, Easton, Pa. (1960).

R. T. Sanderson, CHEMICAL PERIODICITY, Reinhold Publishing Corp., New York (1960), presents many facts arranged in periodic fashion. Binary inorganic compounds are extensively treated.

W. L. Jolly, THE CHEMISTRY OF NON-METALS, Prentice-Hall, Inc., Englewood Cliffs, N. J. (1966) (paperback). Preparation, properties and uses of noble gases, halogens, plus oxygen and nitrogen families.

Films

For ordering information see the *List of Film Sources* at the back of the Teacher's Guide.

CHEMICAL FAMILIES

A CHEM Study film, 1962
16 mm—color

Running Time: 20 minutes

This film, made in collaboration with Drs. J. A. Campbell and J. L. Hollenberg, provides direct experimental support for this chapter. It was produced because the absence of chemistry of the noble gases is inherently difficult to demonstrate convincingly and because the chemistry of the alkali metals and the halogens is hazardous. Some of the content of the film is susceptible to classroom demonstration, but, owing to the excellent, close-up color views provided by the film, the demonstration is probably less effective.

Samples of most of the elements are shown, and the great differences among them are demonstrated. Ordering is begun by segregating metals and nonmetals on the basis of electrical conductivity. Then the gases are further subdivided according to reactivity, thus singling out the noble gas family. Thereafter, the film focuses on actual laboratory demonstrations of the chemistry of the alkalies and the halogens, following closely the development in the Textbook.

The narration will use the term "inert gas" where we have employed "noble gas."

Background Discussion

The Form of the Periodic Table

A great many forms of the Periodic Table have been published, employing concentric circles, stair-steps, and helical arrangements. Each physical arrangement has advantages for displaying

the regularity of a particular property, but the *long form* used in this course was selected because it best fits the needs of most practicing chemists.

The table is arranged into *rows* and *columns*. The first row contains 2 elements; the second row, 8; the third row, 8; the fourth row, 18;

the fifth row, 18; the sixth row, 32; and the seventh row is incomplete. The nuclei of the atoms of the seventh-row elements are unstable. None of the elements beyond uranium, number 92, occurs naturally in recoverable quantities.

The elements in a single vertical column of the table constitute a *chemical group*, or *family*. Some groups, or families, are given names; for example, the alkali elements and the halogen family. Sometimes the groups are identified by a *group number*, as shown on your wall chart of the Periodic Table. Unfortunately, different systems of numbering are in common use. To avoid misunderstanding, name the families rather than number them.

The Rule of Eight

In traditional high school chemistry courses a major emphasis in chemical bonding has been given to the "rule of eight." This rule, based on the presence of eight electrons in the outer

energy levels, may work for the second and third rows of the Periodic Table, but not for hydrogen in the first row or for the elements beyond argon. Indeed, we find that the rule of eight does not hold for some compounds in the second and third rows, such as phosphorus pentachloride (PCl_5), and for such compounds as sulfur tetrachloride (SCl_4) or sulfur hexafluoride (SF_6). Do not teach this rule. Wait for orbital and other representations (Chapter 10). Instead, stress the special stability of the noble gas population.

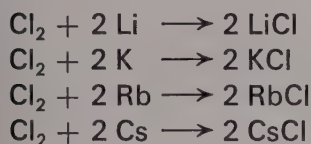
A fuller discussion of chemical bonding will occur in later chapters. For the present, we shall restrict ourselves to interpretations of bonding which have rather general application. In a number of introductory courses, ionic bonding has been given undue emphasis. We shall limit our application of this concept to substances in which the presence of ions is clearly indicated. Both ionic and covalent bonding will be discussed in terms of electrons attracted to two positive nuclei.

Answers to Exercises and Problems

Exercise 7-1

Write the four equations for the reactions between chlorine and lithium, potassium, rubidium, and cesium.

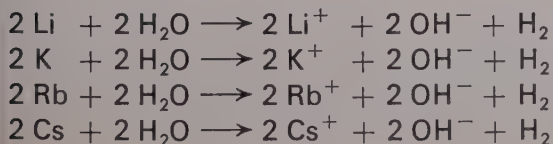
Answer



Exercise 7-2

Write the four equations for the reactions between water and lithium, potassium, rubidium, and cesium.

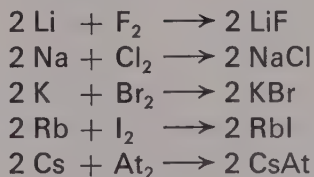
Answer



Exercise 7-3

Write the equations for the reactions between each alkali metal and the halogen which is in the same row of the Periodic Table.

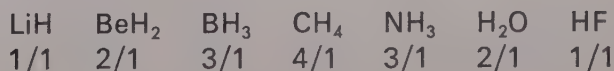
Answer



Problem 1

Write the molecular formulas of the hydrogen compounds of the second-row elements, Li, Be, B, C, N, O, F, Ne. Indicate, for each compound, the H/M atom ratio.

Answer



Neon is not known to form compounds with hydrogen. The compound BH_3 has not been isolated, but B_2H_6 is well known, with the same H/B ratio, 3.

Problem 2

What is the significance of the trends in the boiling temperatures and melting temperatures of the noble gases in terms of attractions among the atoms?

Answer

Both the melting temperatures and boiling temperatures increase from helium to radon. The attractive forces must be increasing as we move down in the Periodic Table.

Problem 3

Why is argon used in many electric light lamps?

Answer

Argon is used because it is inert and does not

react with the tungsten. Thus, the presence of argon insures a longer life for the electric light bulb. In addition, the presence of a gas makes it possible for the filament to lose more heat, hence remain cooler.

Problem 4

Which of the following is NOT a correct formula for a substance at normal laboratory conditions?

- | | |
|------------------------------------|---------------------------------------|
| (a) $\text{H}_2\text{S}(\text{g})$ | (d) $\text{NaNe}(\text{s})$ |
| (b) $\text{CaCl}_2(\text{s})$ | (e) $\text{Al}_2\text{O}_3(\text{s})$ |
| (c) $\text{He}(\text{g})$ | |

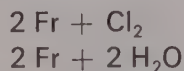
Answer: (d).

Problem 5

Use the information in Table 7-8, page 112, to prepare a column listing the properties of element 87, francium. Give balanced equations for some chemical reactions expected for francium.

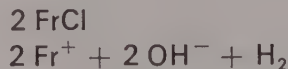
Answer to Problem 5

<i>Francium</i>	Predicted
Position in numerical order	87
Molar mass, g	220
Boiling temperature, °C	650–700
Melting temperature, °C	20–30
Density at 20°C, g/ml	2.5
Ionization energy, kcal/mole	80



Extrapolate molar masses or the ratio of molar mass to order number.

$$\left[\begin{array}{c} \text{extrapolation of values} \\ \text{in Table} \\ 7-8 \end{array} \right]$$



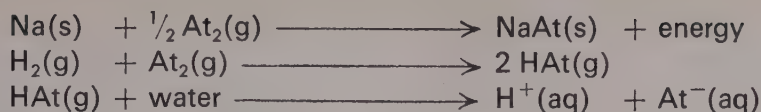
Problem 6

Use the information in Table 7-9, page 115, to prepare a column listing the properties of element 85, astatine. List some chemical reactions expected for astatine.

Answer to Problem 6

<i>Astatine</i>	Predicted
Position in numerical order	85
Molar mass, g	216
Molecular formula	At_2
Boiling temperature, °C	300–400
Melting temperature, °C	200–300

(analogy to Cl_2 , etc.)
(extrapolation of other members)
(extrapolation of other members)

**Problem 7**

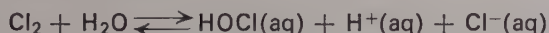
How do the trends in physical properties for the halogens compare with those for the noble gases? Compare boiling temperatures, melting temperatures, and ionization energies.

Answer

Consider that we are moving down (to higher order number) in each column. The first two properties increase and the third decreases for both groups of elements. Each halogen has a higher boiling temperature, a higher melting temperature, and lower ionization energy than its neighboring noble gas.

Problem 8

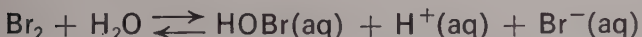
Chlorine is commonly used as a germicide in swimming pools. When chlorine dissolves in water, it reacts to form hypochlorous acid,



Predict what happens when bromine, Br_2 , dissolves in water. Write the equation for the reaction.

Answer

Assuming similar chemistry, we would expect bromine to react, forming hypobromous acid, HOBr .

**Problem 9**

From the following experimental information, identify which chemical family and which element is described. Answer each part separately.

Identify the specific element as soon as possible.

Element A :

- (a) has an ionization energy of more than 400 kcal/mole.
- (b) is a gas at room temperature.
- (c) reacts readily with element number 11 to form an ionic solid.
- (d) has the highest ionization energy of any element in the family.

Element B :

- (a) has an ionization energy less than 400 kcal/mole.
- (b) has a boiling temperature above 800°C .
- (c) reacts with certain elements to form ionic solids.
- (d) reacts with hydrogen in a one to one ratio.

- (e) reacts with water to liberate hydrogen gas.
- (f) has the lowest molar mass and density of any element in the family.

Element C :

- (a) does not form a hydride.
- (b) has a boiling temperature below 25°C .
- (c) has an ionization energy less than 300 kcal/mole.
- (d) forms compounds with both fluorine and oxygen.

Answer

The student is to answer Problems 9 and 10 by using the data in Tables 7-6, 7-8, and 7-9.

Element A :

- (a) Halogen or noble gas could have ionization energy greater than 400 kcal/mole.
- (b) Halogen or noble gas is gaseous.
- (c) Halogen reacts readily with element 11.
- (d) Fluorine has the highest ionization energy among halogens.

Element B :

- (a) Alkali, halogen, or noble gas could have ionization energy below 400 kcal/mole.
- (b) Only alkali metals have boiling temperatures above 800°C .
- (c) Alkali or halogen react with certain elements to form ionic solids.
- (d) Alkali or halogen react with hydrogen in a one to one ratio.
- (e) Alkali reacts with water to liberate $\text{H}_2(\text{g})$.
- (f) Lithium has the lowest molar mass in its family.

Element C :

- (a) Noble gas
- (b) Halogen or noble gas
- (c) Halogen or noble gas
- (d) Xenon

Problem 10

Follow the instructions for Problem 9.

Element D :

- (a) is a solid at room temperature.

- (b) reacts with certain elements to form ionic solids.
- (c) forms a hydride.
- (d) does not react with water.

Element E:

- (a) is a good conductor of electricity.
- (b) melts at a temperature a few degrees above 25°C.
- (c) has a low ionization energy.

Element F:

- (a) readily forms a gaseous hydride.
- (b) the hydride reacts with water to form an acidic solution.
- (c) reacts with hot alkali metals to form an ionic solid.
- (d) has the lowest boiling temperature and the highest ionization energy of any element in the family.

Answer

Element D:

- (a) Alkali or iodine
- (b) Alkali or iodine
- (c) Alkali or iodine
- (d) Iodine

Element E:

- (a) Alkali
- (b) Cesium
- (c) Cesium

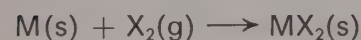
Element F:

- (a) Halogen
- (b) Halogen
- (c) Halogen
- (d) Fluorine

Problem 11

The metals of the second column of the Periodic Table combine with the halogens to form ionic solids. Write a general equation to represent these reactions using M for the metals and X for the halogens.

Answer



Problem 12

Use Table 7-4 and the Periodic Table to suggest formulas for compounds of the following pairs of elements.

- (a) strontium-sulfur
- (b) gallium-fluorine
- (c) beryllium-tellurium
- (d) chlorine-iodine
- (e) arsenic-bromine

Answer

- (a) SrS
- (b) GaF₃
- (c) BeTe
- (d) ICl
- (e) AsBr₃

Problem 13

The metallic elements Na, Mg, and Si in row 3 of the Periodic Table have atomic radii of 1.9, 1.60, and 1.3 Å. Estimate the size of an aluminum atom in a metal sample.

Answer

From a graph of radius vs. row number interpolate

$$\text{Al radius} = 1.4 \text{ Å}$$

The experimental value is 1.4 Å.

Problem 14

The size of an atom can be expressed as the closest distance of approach by another atom. For the halogens the values are: F, 1.35; Cl, 1.80; and Br, 1.95 Å. Estimate the value for iodine.

Answer

From a graph of size vs. molar mass extrapolate to I size, 2.4 Å. The experimental value is 2.2 Å.

Problem 15

The heat of vaporization of some elements in row 5 of the Periodic Table are: Y, 94; Zr, 139; Mo, 142; Tc, 138; Rh, 118; and Ag, 61 kcal/mole. Estimate values for Nb, Pd, and Ru.

Answer

Plot a graph of heat of vaporization vs. atomic mass. The estimated values and experimental values are

element	heat of vaporization, kcal/mole	
	estimated	experimental
niobium	150	166
ruthenium	130	136
palladium	90	90

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

1. Predict the formulas for the bromides of the element in the third row of the Periodic Table. Start with sodium.

Answer

NaBr, MgBr₂, AlBr₃, SiBr₄, PBr₃, SBr₂, ClBr.

2. Write the equations for the following reactions:

- (a) Rubidium with bromine;
- (b) Rubidium with water;
- (c) Strontium with bromine;
- (d) Bromine with hydrogen gas.

Answer

- (a) $2 \text{Rb(s)} + \text{Br}_2(\text{l}) \rightleftharpoons 2 \text{RbBr(s)}$
- (b) $2 \text{Rb(s)} + 2 \text{H}_2\text{O(l)} \rightleftharpoons 2 \text{Rb}^+(\text{aq}) + 2 \text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$
- (c) $\text{Sr(s)} + \text{Br}_2(\text{l}) \rightleftharpoons \text{SrBr}_2(\text{s})$
- (d) $\text{Br}_2(\text{l}) + \text{H}_2(\text{g}) \rightleftharpoons 2 \text{HBr(g)}$

3. Which of the following statements is FALSE? Elements in the first column of the Periodic Table

- (a) are called alkali elements;
- (b) form compounds with oxygen;
- (c) form hydrides of formula MH₃;
- (d) have decreasing melting temperature as the order number goes up;
- (e) react vigorously with chlorine.

Answer: (c).

4. Use Table 7-3 to predict the formula of gallium chloride.

Answer

GaCl₃ from the oxide formulas given.

5. Identify the element which is colored, has an ionization energy between 250 and 300 kcal/mole, and boils above room temperature.

Answer

Br₂ is red, IE = 273 kcal/mole, boils at 58.8°C.

6. Which of the following is NOT a reasonable formula:

- (a) ICl
- (b) XeCl₄
- (c) K₂S
- (d) LiBr₂
- (e) Br₂

Answer: (d).

7. What is the name of the element that has the following properties?

- (a) It is a solid at room temperature.
- (b) It is a nonmetal.
- (c) It forms an ion with 1 – charge.
- (d) Its gaseous molecule is diatomic.

Answer: Iodine.

8. What is the name of the element that has the following properties?

- (a) It ranks high according to relative abundance in the earth's crust.
- (b) It is a rather common metal.
- (c) It forms an oxide with the formula M₂O₃ in which M is the symbol for the element.

Answer: Aluminum.

9. The distance of nearest approach for unbonded atoms in the oxygen family are: O, 1.40 Å, S, 1.85 Å, and Te, 2.2 Å. Estimate the value for Se.

Answer

About midway between S and Te; 2.0 Å.

10. Given these values of density, use the Periodic Table to estimate the density of niobium (Nb, number 41) and tantalum (Ta, number 73).

V	5.96 g/ml	Co	8.9 g/ml
Nb	?	Rh	12.5
Ta	?	Ir	22.4

Answer

Vanadium, Nb, and Ta occupy the column four to the left of Co, Rh, and Ir. Since there are trends across the rows of the table, there should be some relation between the densities of these elements. The density of V is about $\frac{2}{3}$ that of Co. Using this ratio gives

$$\text{Nb density} = \frac{2}{3} (12.5) = 8.6 \text{ g/ml}$$

$$\text{Ta density} = \frac{2}{3} (22.4) = 15.0 \text{ g/ml.}$$

A student might also say that Co density is 3 g/ml greater than V, therefore

$$\text{Nb density} = 12.5 - 3 = 9.5 \text{ g/ml}$$

$$\text{Ta density} = 22.4 - 3 = 19.4 \text{ g/ml}$$

Either set is a reasonable estimate.

11. Use Tables 7-6 to 7-9 to find evidence that

the attractive forces are similar in fluorine gas and argon gas.

Answer

The boiling temperatures of F_2 and Ar are nearly the same.

12. Write formulas for a reasonable compound of each pair of elements given. The order numbers in parenthesis will help you locate them in the Periodic Table.

aluminum (13) tellurium (52)

tin (50) chlorine (17)

germanium (32) oxygen (8)

selenium (34) iodine (53)

antimony (51) hydrogen (1)

Answer

Al_2Te_3 SnCl_4 GeO_2 SeI_2 SbH_3

The Structure of the Atom



Intent and Approach

This chapter reviews many of the types of evidence that contribute to our belief in the usefulness and applicability of the atomic theory. The use of these bits of evidence to deduce our current ideas of atomic structure is the important thing here. The types of evidence are, generally, outside the students' experience. The experiments must be described, the results cited, and the significance given in an authoritarian way. Nevertheless, this chapter is consistent with the experimental philosophy of this course, since the

student is to be reminded that experiments provide the basis for every aspect of the atomic theory and every detail of the structure of the atom.

The totality of this evidence, together with the "garbage collector" analogy (p. 131 in this Guide), provides an excellent sample of how a scientific view, or theory, gains general acceptance. Consistency with a variety of different types of experimental evidence establishes confidence in a theory. Seldom can one behavior be singled out as *the* decisive evidence.

Outline

The gas discharge tube is brought up in the introduction and leads to a study of light (8-1).

The wave nature, characteristic frequency, wavelength, and energy are discussed first. Then simple spectrographs and spectra are examined.

The electron is identified by its behavior in discharge tubes (8-2). The charge and mass were determined by Thomson and Millikan.

The proton was found by additional study of discharge tube behavior (8-3).

A detailed model of the atom was put forward by Thomson (8-4). Though later discarded, it was an important step.

X rays and radioactivity provided a way (α -particles) to probe the internal structure of the atom (8-5).

Rutherford used the results of α -scattering to deduce a nuclear atom (8-6).

Atomic number also came from α -scattering experiments (8-6).

The neutron completes the list of major subatomic particles. Isotopes result when nuclei with the same number of protons contain differing numbers of neutrons (8-7).

A review completes the chapter (8-8).

New Concepts

1. Light extends beyond the visible spectral range: gamma rays, X rays, ultraviolet, infra-

red, and microwave frequencies are all part of the light spectrum.

2. Light is characterized by wavelength and frequency.
3. Electrons, protons, and neutrons are subatomic particles deduced from the behavior of matter under the influence of various forces.
4. The nuclear atom.
5. Isotopes, X rays, and radioactivity are mentioned briefly.

SCHEDULE AND RELATED MATERIAL

Suggested Time: 8 days

Text Section	Topic and Related Work	Exercises	Problems		
			Easy	Medium	Hard
	Expt. 21. Construction of a Logical Model				
8-1	Light, Spectra Demo. 24. Spectra and Absorption Demo. 25. Line Spectra	1	2	1	
8-2	The Electron			4	3
8-3	The Proton		5	6, 12	
8-4	Thomson Atom				
8-5	X rays and Radioactivity				
8-6	Rutherford Atom		7, 9	8, 13-15*	10, 11
8-7	The Neutron, Isotopes		17, 18	16, 19-21	
8-8	Review Expt. 22. Qualitative Analysis; Ag^+ , Hg_2^{2+} , Pb^{2+} fits anywhere.				

* Problems 13-15 should be assigned as a unit.

Development

This chapter is intended to provide a firm foundation for the belief that most students have in atoms. This belief, planted by early science courses and nurtured by outside sources, is usually rather vague and is almost always instilled through a completely authoritarian approach. The student believes there are atoms, but has no experimental basis for this tenet. In opening the chapter, set up the logical mechanism by which belief in an unseen object can have foundation. All students wonder how we can know about atoms without being able to see them. You can attack this question by presenting the "garbage collector" analogy given below and by means of

Experiment 21.

The "garbage collector" analogy gives a consistent set of familiar observations that display the general pattern. Observations concerning the unseen object are collected, and various theories are compared on the basis of consistency with the observations. Experiment 21 lets the student try this pattern via observations on a physical system which he cannot see. The "black box" experiment forces the student to form a picture of an object on the basis of indirect observations. This is exactly analogous to our attempts to form a picture of the atom.

The Garbage Collector Analogy

The following story illustrates, *in nonscientific terms*, the deductive process which is the basis of knowledge gained by scientific method. It is an important concept which every student should carry away from the course.

A new tenant is told by his neighbor that the garbage collector comes every Thursday, early in the morning. Later, in answer to a question from his wife about the same matter, the tenant says, "I have been told there is a garbage collector and that he comes early Thursday morning. We shall see if this is true." The tenant, a scientist, accepts the statement of the neighbor (who has had opportunity to make observations on the subject). However, he accepts it *tentatively* until he himself knows the evidence for the conclusion.

After a few weeks, the new tenant has made a number of observations consistent with the existence of a Thursday garbage collector. Most important, the garbage does disappear every Thursday morning. Second, he receives a bill from the city once a month for municipal services. And there are several supplementary observations that are consistent—often he is awakened at 5:00 a.m. on Thursdays by a loud banging and sounds of a truck. Occasionally the banging is accompanied by gay whistling, sometimes by a dog's bark.

The tenant now has many reasons to believe in the existence of the garbage collector. Yet he has never seen him. Being a curious man and a scientist, he sets his alarm clock one Wednesday night to ring at 5:00 a.m. Looking out the window Thursday morning, his first observation is that it is surprisingly dark out and things are difficult to see. Nevertheless, he discerns a shadowy form pass by, a form that looks like a man carrying a large object.

Seeing is believing! But which of these pieces of evidence really constitutes "seeing" the garbage collector? Which piece of evidence is *the* basis for "believing" there is a garbage collector? The answer is, *all* of the evidence taken together constitutes "seeing." And *all*

of the evidence taken together furnishes the basis for accepting the "garbage collector theory of garbage disappearance." The direct vision of a shadowy form at 5:00 a.m. would not constitute "seeing a garbage collector" if the garbage didn't disappear at that time. (The form might have been the paper boy or the milkman.) Neither would the garbage disappearance alone consist of "seeing" the garbage collector. (Perhaps a dog comes by every Thursday and eats the garbage. Remember, a dog's bark was heard!) No, the tenant is convinced there is a garbage collector because the assumption is consistent with so many observations, and it is inconsistent with none. Other possible explanations fit the observations too, but not as well (the tenant has never heard a dog whistle gaily). The garbage collector theory passes the test of a good theory—it is useful in explaining a large number of experimental observations. This was true even before the tenant set eyes on the shadowy form at 5:00 a.m.

You may want to ask some questions to bring out things the tenant does *not* know about the collector:

- Is the collector a man or woman?
- What age is he?
- What does he smoke—pipe, cigar, or cigarette?
- What path did he walk?
- Does the same one come every Thursday?

These questions will establish that many details are not explained by the model. They will also help condition the student to accept the situation that our orbital model (Chapter 9) does not tell us the path of the electron or its exact speed at any instant.

See p. 137 for some remarks on the difficulty of "proving" a hypothesis.

Expt. 21, CONSTRUCTION OF A LOGICAL MODEL,

fits here. See p. 110 in the Laboratory Guide.

8-1 Light

Demo. 24, SPECTRA AND ABSORPTION,

fits with p. 124. See p. 114 in the Laboratory Guide.

Light is related to energy and is then likened to a water wave. Meaning can be added by considering the electric field near an electron that is moved up and down with a regular periodic motion. The resultant oscillating electric field radiates at the speed of light. Another electron at some distance from the first responds to the oscillating electric field, taking up the same periodic motion as the first electron. These two electrons furnish a useful model for demonstrating the emission of light (the first electron) and the absorption of light (the second electron).

By an extension of the water wave analogy, it is reasonable to associate different colors with different frequencies. Furthermore, the idea that the human eye is not sensitive to all frequencies is readily grasped. For the explanation of the hydrogen atom spectrum in Chapter 9, we want the student to understand that different frequencies mean different energies.

The details of a spectrograph are not important. However, the observation of the hydrogen, or other, spectrum is instructive.

Demo. 25, LINE SPECTRA,

fits here. See p. 116 in the Laboratory Guide.

8-2 The Discovery of the Electron

8-3 The Discovery of the Proton

The presentation of the gas discharge experiments is kept simple. You might make the point that light cannot be deflected by electrical or magnetic fields (of magnitude available in 1900–1920).

Gas discharge experiments, as well as those described in the next four sections, provide some elements of “seeing” the atomic particles. Help the student see how the evidence is used to deduce atomic structure in the same way the

tenant deduced the presence of the garbage collector.

First, the glowing spot is directly visible. Second, it is easy to imagine an invisible stream of particles hurtling through the hole in the electrode to crash against the fluorescent screen in a burst of light. Third, the experiment conveys detailed information about these particles, information difficult to obtain any other way. The electric charge on a particle is clearly evident from the deflection experiments. Accurate measurements of such deflections even lead to a measure of the ratio of electron charge to electron mass.

Yet there is a real difference between this experiment and the “direct vision” of the shadowy form of the garbage collector. We don’t see the electron directly; rather we see a burst of light on the fluorescent screen. The light isn’t considered to be the electron: the burst of light is caused by molecular damage to the screen—damage resulting from the electron crash. A more apt comparison from our analogy would be our seeing some footprints in the garden. We assume the footprints are caused by the garbage collector. Then from certain properties of the footprints—size, depth, spacing—we form a detailed image of his height, weight, stride. You will find that this is typical of most of the experiments that might be called “seeing” atoms and their components. We see their “footprints”—bursts of light on a screen, marks on a photographic plate, discharges in a Geiger counter, etc. These “footprints” substantiate in every way the atomic theory and furnish detailed information on the nature of atoms.

The Ratio of Electron Charge to Electron Mass, e/m

The general outline of Thomson’s determination of e/m is as follows. A beam of electrons passes through the positive electrode and strikes the far end of the tube, producing a fluorescent spot. When the magnetic field is turned on (by passing current through the coil), the fluorescent spot moves. Using an electromagnet, rather than the simple horseshoe shown in Textbook Figure 8-6, allows control of the field. The spot

moves because a charged particle moving in a uniform magnetic field has a path which is a portion of a circle. From the deflection of the spot and the length of the apparatus, the radius of this circular path can be determined. This radius we shall call r .

This radius is related to the mass, m , charge, e , velocity, v , of the electron, the strength of the magnetic field, B , as follows:

$$r = \frac{m}{e} \times \frac{v}{B} \quad (1)$$

This equation shows that the greater the mass or velocity of the particle, the less curved is its path (a small value of r describes a highly curved path). On the other hand, the path of the particle becomes more curved if the magnetic field is made stronger.

We can rearrange equation (1) to the form

$$\frac{e}{m} = \frac{1}{r} \times \frac{v}{B} \quad (2)$$

Equation (2) shows us how to calculate the charge/mass ratio for the electron if r is measured and both v and B are known.

However, the velocity, v , of the electron is still unknown. We must calculate this quantity from the work done on the electron as it was accelerated, moving from the negative electrode to the positive electrode. The work done on the electron is the product of the charge on the electron times the voltage difference, V , between the electrodes:

$$\text{Work done on electron} = e \times V \quad (3)$$

This work is used to accelerate the electron, giving it kinetic energy. Also, we know that the kinetic energy of the electron can be expressed in terms of its mass and velocity:

$$\text{Kinetic energy of a moving electron} = \frac{1}{2}mv^2 \quad (4)$$

We must equate (3) and (4): the work done equals the kinetic energy the electron acquires:

$$eV = \frac{1}{2}mv^2 \quad (5)$$

The voltage, V , we obtain from a voltmeter reading.

Expressions (2) and (5) both relate the ratio e/m to the electron velocity and the measured quantities, r , B , and V . We can calculate e/m if v is eliminated from the two equations. This is an algebraic process that can be done several ways. Here is one way.

Since (5) involves v^2 , let us square expression (2):

$$\frac{e^2}{m^2} = \frac{v^2}{r^2B^2} \quad (6)$$

Now let us multiply both sides of (6) by m/e :

$$\frac{e}{m} = \frac{mv^2}{e} \times \frac{1}{r^2B^2} \quad (7)$$

Now we can rearrange (5) to the form

$$\frac{mv^2}{e} = 2V \quad (8)$$

And, finally, we can substitute (8) into (7):

$$\frac{e}{m} = \frac{mv^2}{e} \times \frac{1}{r^2B^2} = 2V \times \frac{1}{r^2B^2}$$

or

$$\frac{e}{m} = \frac{2V}{r^2B^2} \quad (9)$$

We measure V (from the voltmeter reading), r (from the deflection of the spot), B (from the current through the magnet coil windings), substitute them into (9), and calculate

$$\frac{e}{m} = 1.759 \times 10^8 \frac{\text{coulombs}}{\text{gram}}$$

8-4 The Thomson Model for the Atom

This section is naturally very short because this was an unsuccessful model. You can draw the comparison to the child's regularity "cylindrical objects burn." In the real case, however, the Thomson model was the best available for 8 years (1903–1911).

8-5 The Discovery of X rays and Radioactivity

This section is a slight detour to pick up the thread of work which eventually led to Rutherford's ex-

periments. This thread leads from Röntgen's discovery of X rays to the natural radiations of some elements. The particular ones giving α -particle emission bring us to the stage at which Rutherford could make his α -scattering experiment.

These matters are deliberately treated in an extremely brief manner. They are a side issue. The interesting aspects of radiochemistry will be explored in Chapter 21. Do not be drawn into them now.

8-6 The Rutherford Model of the Atom

This section can be introduced with a nonscientific analogy. Present this before the student reads the section. Suppose you are invited into a completely dark room, handed some phosphorescent tennis balls, and asked to throw them straight into the darkness. Further, you were asked to explain any observations. Let us say the first eleven balls just sail through the darkness and out of sight. Then the next ball changes course after about 25 feet. It angles to the right. After four more tosses that have no path changes, the 17th toss again shows a sharp angle in the flight line. Repeated tosses continue to develop this pattern; most balls pass straight through, but a few are deflected, some drastically. How would you explain these results?

The student should see the connection to Experiment 21 (Logical Models) and, after he reads about α -scattering, to Rutherford's experiment. The example above should help clarify the interpretation leading to the nuclear atom.

The significance of the Rutherford experiment

escapes some students. The Thomson model of the atom provides an intuitively reasonable basis for the expectation that bombarding particles would be reflected, since there are obviously no "holes" between the atoms. What it does *not* do, however, is provide a reasonable basis for explaining why most of the bombarding particles penetrate almost undeflected and only a few reflect back toward the source. Thus the penetrating particles are as important in this experiment as the reflected particles.

Since the student already has been using the atomic theory, it will require some emphasis to make sure he recognizes that the results in these sections, which seem to *follow* from the atomic theory, actually form the basis for the theory—that is, the atomic theory follows from the experiments.

The determination of atomic number is also mentioned as a result that comes from α -scattering. These brief remarks begin the connection between atomic structure and the Periodic Table. Chapter 9 will develop this theme to a considerable extent.

8-7 The Neutron and Isotopes

The neutron is added as the third major subatomic particle so that the mass of individual atoms can be understood. Isotopes follow naturally. Again, this topic will receive further attention in Chapter 21. At this stage, bring the student to understand that the nuclei vary in mass but that the chemical reactions are fixed by the number of electrons. He will find in the next chapter how important the electron arrangement is.

Supplementary Material

Books

J. J. Lagowski, *THE STRUCTURE OF ATOMS*, Houghton-Mifflin Co., Boston, 1964. A paperback covering the gas discharge experiments, the nuclear atom, and

other topics on atomic structure.

E. Ruechardt, *LIGHT*, Univ. of Michigan Press, Ann Arbor, 1958, a paperback.

Background Discussion

Subatomic Particles

These details of how the particles were charac-

terized are for your use only. Do not elaborate greatly on the Textbook here. We have already considered two charged particles, the electron

and the proton. These have masses smaller than that of the lightest atom, the hydrogen atom. Deflection experiments show that the mass of slow-moving (charge $1-$) electrons is $1/1840$ that of the hydrogen atom. The mass of the proton (charge $1+$) is substantially equal to the mass of the hydrogen atom. The difference is the mass of an electron. Thus the mass of the hydrogen atom is equal to the combined masses of one proton and one electron.

No negatively charged particle lighter than the electron has been discovered. In 1932, C. A. Anderson, an American physicist, discovered a transitory, positively charged particle having the same mass as the electron. This particle, usually called the positron, but sometimes the positive electron, exists independently only for very short periods of time. Since, in chemistry, we are interested in more stable particles, we shall not need to consider the positron here. A number of other particles, called mesons, are formed in bombardment reactions involving very high energy. Mesons have masses between that of the electron and that of the proton; some have no charge, and others have a charge of $1-$ or $1+$. The mean lifetime of a meson is only about 10^{-6} second. Mesons, like the positron, play no significant role in chemistry.

Another particle, discovered in 1932 by James Chadwick, an English physicist, is important to us. It is the *neutron*, a neutral particle having approximately the same mass as the proton. It is hard to detect and control (because it has no charge). Its mass is made evident by the effect it produces when it collides with atoms.

Beams of Matter

Much of the evidence for atoms and molecules comes from the behavior of beams of matter. These behave as if they are made up of individual particles having definite masses and individual speeds.

As is true of light beams, beams of matter travel in straight lines until deflected. Neither beams of light nor beams of neutral matter change speed or direction when subjected to electric or

magnetic fields, but beams of charged matter are affected. Charged beams act as if they consist of charged particles, each responding to electric and magnetic fields in the same way that visible charged bodies are known to respond. The mass of the particles is found to be that of the chemist's atoms and molecules.

Charged beams, both positive and negative, can be produced in evacuated tubes. The negative beams, regardless of the nature of the electrodes, all show highly curved paths corresponding to a single value of e/m .

$$e/m = 1.76 \times 10^8 \text{ coulombs/g}$$

These particles are called electrons. Their charge (the electron charge) has been evaluated independently as 1.60×10^{-19} coulomb. Thus the electron mass (at nonrelativistic speeds) is 9×10^{-28} gram.

All positively charged beams show much smaller deflections. The most easily deflected beams (of charged hydrogen atoms) have an e/m ratio which is $1/1840$ that of the electron. If the particles in the hydrogen beam carry a charge equal in magnitude (but opposite in sign) to the electron charge, their masses are 1840 times the electron mass. Beams of H^+ ions are proton beams. All other positive beams show even less deflection; their masses must be correspondingly greater than the proton mass, since no charge smaller than the proton charge or the electron charge has been found.

The positive beams obtained from different gases were studied by J. J. Thomson, who found that *the masses are those predicted by the atomic theory for the atoms and molecules* and that *the masses are approximately whole numbers on the atomic mass scale, based on 16 for the oxygen atom*. Later experiments showed that substances whose atomic masses differ substantially from whole numbers give two or more e/m values in which each mass has approximately an integral value. Such substances are mixtures of isotopes. The atoms of each isotope have the same mass number.

The mass spectrograph is an instrument designed especially to give very precise values for

e/m , and hence for atomic masses. It can separate atoms of two elements having the same mass number but slightly different exact masses. The hydrogen isotope ^3H has the mass 3.017029, whereas the helium isotope ^3He has the mass 3.017016.

All negative beams other than electron beams undergo small deflections similar to those of positive beams. These beams may be explained in terms of negatively charged atoms and molecules, just as positive beams are explained by positively charged atoms and molecules.

The Nuclear Atom

The nuclear theory of the atom was proposed by E. Rutherford in 1911 on the basis of the scattering experiment described. Rutherford's explanation of his scattering data was that the mass of the atom and all the positive charge of an atom are concentrated in a tiny nucleus and that electrons occupy the space in the atom around the nucleus.

This theory laid the basis for modern atomic structure. It leaves open several questions:

1. What is the internal structure of the nucleus?
2. How are the electrons arranged around the nucleus?
3. How do the atoms of different elements differ in structure?

The first question is still unanswered and is the subject of intensive research by nuclear scientists. At present we employ certain rules which lead to the observed charges and masses of nuclei. We are much less certain about the structure of the nucleus than about other details of atomic structure.

The second question will be considered throughout the rest of the course (especially Chapter 9). It is very closely tied to chemistry. We shall now consider the third question.

Isotopes

Different forms of an element were first recognized in the products from radioactive disintegration of atoms. The British chemist F. Soddy,

in 1913, called the different forms isotopes (isotopes occupy the same place, chemically, in the Periodic Table).

The separation of isotopes was first accomplished in the same year, when J. J. Thomson found that neon gas contained two kinds of atoms having masses 20 and 22. He found no atoms having masses 20.2, the average mass of the atoms. All other elements whose molar masses depart substantially from whole numbers consist of a mixture of two or more kinds of atoms. All the isotopic atoms have the same nuclear charge; they differ in mass number. The element neon consists mainly of two isotopes, neon-20 (^{20}Ne) and neon-22 (^{22}Ne). The mass numbers are used to identify the different species of atoms in an element.

Thus we see that it is the atomic number rather than the mass that identifies an element. The atomic number characterizes an element precisely; the molar mass does not.

Some elements—for example, fluorine, sodium, aluminum, phosphorus, all of which are odd-numbered elements—have only one naturally occurring nuclear species. Most elements have two or more naturally occurring isotopes; tin has ten. About 300 naturally occurring nuclear species are known for the first 92 elements, and more than 1000 have been made in nuclear bombardment reactions. Isotopic species have been made and identified for all the elements.

Electrons in Atoms

Because all the atoms of an element have the same nuclear charge, they must have the same number of electrons in the neutral atom. These electrons surround the nucleus in a manner which in some aspects, but not all, resembles an electron cloud. It is the electron cloud of an atom that is primarily responsible for the chemical behavior of the atom. Chapters 9 and 10 cover this in detail.

Different isotopes of an element have essentially the same chemical properties because their nuclei have the same charge and their electron clouds have identical form. The isotopes differ

only in those properties that are related to the mass of the atom.

The electrons of an atom are arranged in a series of orbitals in such a way that the inner orbitals are filled. The electrons outside the filled orbitals are the ones that interact most strongly when two atoms are brought together. These outer electrons are called *valence electrons*. They will be discussed and correlated with chemical behavior in later chapters.

The Nature of Proof

Scientists are aware of all of the evidence for atoms discussed in this chapter and of other evidence as well. Yet they do not claim to have *proved* the existence of atoms. The explanation of their attitude lies in the nature of proof. Proof

of a proposal requires more than consistency with all the known evidence; it requires also that the proposal is and will remain the only one that can explain the facts. This guarantee cannot be given. There always remains the possibility that new experiments will produce evidence that will force us to modify or abandon current theories. Since this possibility can never be ruled out completely, scientists are unwilling to make dogmatic assertions claiming final proof. When a scientist says he believes in atoms, he means it is *useful* to believe in atoms. There is a tentativeness in his attitude, however; he stands ready to stop believing in atoms if new evidence were to appear that would make it no longer useful to do so.

Answers to Exercises and Problems

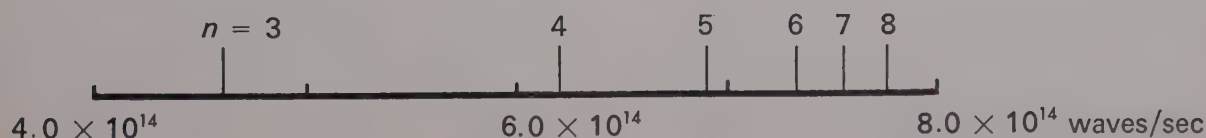
Exercise 8-1

Draw a line 8 cm long on a piece of paper and mark off 2 cm divisions. Label these divisions from 4.0×10^{14} to 8.0×10^{14} waves per second. Use the Balmer formula to calculate ν when $n = 4, 5, 6, 7$, and 8. Draw a vertical mark for each of these frequencies on your frequency scale. Include the value for $n = 3$ calculated in the example above.

Answer

$$\begin{aligned} n = 4\nu &= 3.29 \times 10^{15} \left(\frac{1}{2^2} - \frac{1}{4^2} \right) \\ &= 3.29 \times 10^{15} \left(\frac{3}{16} \right) \\ &= 6.16 \times 10^{14} \text{ waves/sec} \\ n = 5\nu &= 3.29 \times 10^{15} \left(\frac{1}{2^2} - \frac{1}{5^2} \right) \\ &= 3.29 \times 10^{15} \left(\frac{21}{100} \right) \end{aligned}$$

$$\begin{aligned} &= 6.90 \times 10^{14} \text{ waves/sec} \\ n = 6\nu &= 3.29 \times 10^{15} \left(\frac{1}{2^2} - \frac{1}{6^2} \right) \\ &= 3.29 \times 10^{15} \left(\frac{8}{36} \right) \\ &= 7.31 \times 10^{14} \text{ waves/sec} \\ n = 7\nu &= 3.29 \times 10^{15} \left(\frac{1}{2^2} - \frac{1}{7^2} \right) \\ &= 3.29 \times 10^{15} \left(\frac{45}{196} \right) \\ &= 7.54 \times 10^{14} \text{ waves/sec} \\ n = 8\nu &= 3.29 \times 10^{15} \left(\frac{1}{2^2} - \frac{1}{8^2} \right) \\ &= 3.29 \times 10^{15} \left(\frac{15}{64} \right) \\ &= 7.72 \times 10^{14} \text{ waves/sec} \end{aligned}$$



Problem 1

Use the data about water waves on page 124 to calculate how fast the wave is moving, in miles per hour.

Answer

$$\nu \left(\frac{\text{wave}}{\text{sec}} \right) \lambda \left(\frac{\text{feet}}{\text{wave}} \right) = \text{velocity} \left(\frac{\text{ft}}{\text{sec}} \right)$$

$$\left(5 \times 10^{-2} \frac{\text{wave}}{\text{sec}} \right) \left(50 \frac{\text{ft}}{\text{wave}} \right) \times \left(3600 \frac{\text{sec}}{\text{hr}} \right) \left(\frac{1 \text{ mile}}{5280 \text{ ft}} \right) = 17 \text{ miles/hr}$$

Problem 2

The electromagnetic waves used in FM broadcasting by radio or television have frequencies of approximately 100 megacycles per second. In standard AM radio broadcasting, the frequency is approximately 1 megacycle per second.

Use the relationship $\lambda = c/\nu$, where c = velocity of light = 3.0×10^{10} cm/sec, to calculate the wavelengths used in AM and FM broadcasting. Compare these values with the wavelengths for red and blue light in Table 8-1.

Answer

$$\text{for AM } \lambda = \frac{3.0 \times 10^{10} \text{ cm/sec}}{1000 \times 10^3 \text{ cycles/sec}}$$

$$= 3.0 \times 10^4 \frac{\text{cm}}{\text{cycle}}$$

$$\text{for FM } \lambda = \frac{3.0 \times 10^{10} \text{ cm/sec}}{100 \times 10^6 \text{ cycles/sec}}$$

$$= 3.0 \times 10^2 \frac{\text{cm}}{\text{cycle}}$$

Visible light has wavelengths from 4.0×10^{-5} cm/cycle (blue) to 7.0×10^{-5} cm/cycle (red).

Problem 3

The pressure in a gaseous discharge tube is approximately 10^{-2} atmosphere when glow discharge begins. As the pressure is decreased, the cathode dark space increases in length. At about 10^{-6} atmosphere pressure, the glow discharge disappears.

How many molecules would there be in one cubic centimeter of gas when the glow first appears?

How many molecules would there be in one cubic centimeter of gas when the glow disappears?

Answer

At STP,

$$1 \text{ cm}^3 = \frac{1}{22400} \text{ mole}$$

or

$$4.5 \times 10^{-5} \text{ mole}$$

This 1 cm^3 will contain $(4.5 \times 10^{-5})(6.0 \times 10^{23}) = 2.7 \times 10^{19}$ molecules at STP. When glow starts at 0.01 atmosphere there will be 2.7×10^{17} molecules/cm³. When glow disappears at 10^{-6} atmosphere there will be 2.7×10^{13} molecules/cm³.

Problem 4

How many electrons are needed to furnish a mass of one gram? What would be the mass of a mole of electrons?

Answer

$$1 \text{ electron} = 9.11 \times 10^{-28} \text{ g}$$

$$\frac{1}{9.11 \times 10^{-28}} = 1.10 \times 10^{27} \text{ electrons/g}$$

One mole of electrons weighs

$$(9.11 \times 10^{-28})(6.0 \times 10^{23}) = 5.5 \times 10^{-4} \text{ g}$$

Problem 5

How much electric charge is provided by one mole of electrons? By one mole of protons?

Answer

One electron provides -1.60×10^{-19} coulomb.

One mole of electrons gives

$$(-1.60 \times 10^{-19})(6.0 \times 10^{23})$$

$$= -96,000 \text{ coulombs}$$

Note: This calculation does not give 96,500 coulombs (1 Faraday) because we have rounded Avogadro's number.

A mole of protons has the same amount of electrical charge but of positive sign.

Problem 6

From the molar mass of the electron and the molar mass of the hydrogen atom, calculate the molar mass of the proton. Calculate the ratio of proton mass to electron mass.

Answer

A hydrogen atom has one electron and one proton. Hence, one mole of hydrogen atoms contains a mole of each particle.

Molar mass of the proton = $1.008 - 5.5 \times 10^{-4}$
= 1.007 g within the precision given.

$\frac{1.007}{5.5 \times 10^{-4}} = 1830$; the proton is about 1800
times as heavy as the electron.

Problem 7

The nucleus of an aluminum atom has a diameter of about 2×10^{-13} cm. The atom has an average diameter of about 3×10^{-8} cm. Calculate the ratio of the diameters.

Answer

If we let d = the diameter of the nucleus = 2×10^{-13} cm and D = the diameter of the atom = 3×10^{-8} cm, then the ratio is

$$\frac{d}{D} = \frac{2 \times 10^{-13}}{3 \times 10^{-8}} = \frac{2}{3} \times 10^{-5} = 0.7 \times 10^{-5}$$

This expresses the fact that the nucleus is about 1/100,000 as large (in diameter) as the atom. The student may calculate the ratio $D/d = 1.5 \times 10^5$, which is just the other way of looking at it—the atom is about 100,000 times as large as the nucleus.

Problem 8

The radius of a carbon atom in many compounds is 0.77×10^{-8} cm. If the radius of a Styrofoam ball used to represent the carbon atom in a molecular model is 1.5 cm, how much of an enlargement is this?

Answer

$$\frac{1.5 \text{ cm}}{0.77 \times 10^{-8} \text{ cm}} = 2.0 \times 10^8$$

The enlargement factor is 200 million.

Problem 9

Platinum and zinc have the same number of atoms per cubic centimeter. Would thin sheets of these elements differ in the way they scatter alpha particles? Explain.

Answer

Yes. The scattering of alpha particles of moder-

ate energy is determined by the charge on the nucleus. Platinum has the larger nuclear charge, hence will deflect more α -particles through large scattering angles. In this connection, it can be remarked that the mass of the electrons is so low that they offer negligible opposition to an alpha particle, about as much as a one-pound brick gives to a four-ton truck.

Problem 10

Assume that the nucleus of the fluorine atom is a sphere with a radius of 5×10^{-13} cm. Calculate the density of matter in the fluorine nucleus.

Answer

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}(3.14)(5 \times 10^{-13})^3$$

$$= 5.2 \times 10^{-37} \text{ cm}^3$$

$$\text{mass of one atom} = \frac{19.0 \text{ g/mole}}{6.0 \times 10^{23} \text{ atoms/mole}}$$

$$= 3.2 \times 10^{-23} \text{ g/atom}$$

$$\text{density} = \frac{3.2 \times 10^{-23}}{5.2 \times 10^{-37}} = 6.1 \times 10^{13} \text{ g/cm}^3$$

The mass 6.1×10^{13} grams is about that of 50 million cubic yards of dry sand. Imagine all that compressed into one cubic centimeter!

Problem 11

An average dimension for the radius of a nucleus is 1×10^{-13} cm and for the radius of an atom is 1×10^{-8} cm. Determine the ratio of atomic volume to nuclear volume.

Answer

$$\frac{V_{\text{atom}}}{V_{\text{nucleus}}} = \frac{\frac{4}{3}\pi r_{\text{atom}}^3}{\frac{4}{3}\pi r_{\text{nucleus}}^3} = \frac{r_{\text{atom}}^3}{r_{\text{nucleus}}^3} = \frac{(10^{-8})^3}{(10^{-13})^3}$$

$$= \left(\frac{1}{10^{-5}}\right)^3 = 10^{15}$$

The atom has 10^{15} times the volume of the nucleus.

Problem 12

Which would have a larger charge to mass ratio, a Na^+ or a K^+ ion?

Answer

The Na^+ ion would have the larger charge/mass

ratio. Each ratio is determined by dividing the same charge by the mass of the ion. One Na^+ weighs less than a K^+ .

Specifically, for Na^+

$$\text{charge} = 1 \quad \text{mass} = 23.0/6.0 \times 10^{23}$$

$$\frac{\text{charge}}{\text{mass}} = \frac{6.0 \times 10^{23}}{23.0} = 2.6 \times 10^{22} \quad \text{units of charge/g}$$

for K^+

$$\text{charge} = 1 \quad \text{mass} = 39.1/6.0 \times 10^{23}$$

$$\frac{\text{charge}}{\text{mass}} = \frac{6.0 \times 10^{23}}{39.1} = 1.5 \times 10^{22} \quad \text{units of charge/g}$$

The ratio is larger for Na^+ .

Problem 13

Suppose, in the Thomson model for the atom, that the charge of the proton is uniformly spread throughout the volume for one hydrogen atom. Using the value 10^{-8} cm for the radius of the hydrogen atom and 1.6×10^{-19} coulomb for the unit electric charge, calculate the charge density in coulombs/cm³.

Answer

$$\text{Charge density} = \left(\frac{\text{charge}}{\frac{4}{3}\pi r^3} \right) = \left(\frac{\text{charge}}{4.19r^3} \right)$$

$$\begin{aligned} \text{Charge density} &= \left(\frac{1.6 \times 10^{-19} \text{ coulomb}}{4.19(10^{-8})^3 \text{ cm}^3} \right) \\ &= 3.8 \times 10^4 \frac{\text{coulombs}}{\text{cm}^3} \end{aligned}$$

Problem 14

Repeat Problem 13 for the Rutherford model for the hydrogen atom. The proton is now the nucleus of the atom, with a radius of approximately 10^{-13} cm.

Answer

$$\begin{aligned} \text{Charge density} &= \frac{1.6 \times 10^{-19} \text{ coulomb}}{4.19(10^{-13})^3 \text{ cm}^3} \\ &= 3.8 \times 10^{19} \frac{\text{coulombs}}{\text{cm}^3} \end{aligned}$$

Relate the answers to Problems 13 and 14 to Thomson's and Rutherford's models of the atom. Let the much larger value, 10^{19} coulombs/cm³ compared to 10^4 coulombs/cm³, show why Rutherford's model fits the α -scattering experi-

ments. Problem 15 is to lead the student to the answer.

Problem 15

Use your answers from Problems 13 and 14 to discuss qualitatively the scattering of alpha particles by Thomson atoms and by Rutherford atoms.

Answer

The charge is very much more concentrated in the Rutherford model. Therefore an α -particle that came near such a nucleus would experience a large repulsive force. On the other hand, the nucleus is so small, many α -particles would not pass near enough to experience appreciable repulsion.

In the Thomson model of the atom, the charge density is very low, but it is "everywhere." Thus, all α -particles passing through such an atom would be repelled with a small force.

Problem 16

Which of the following statement is FALSE? The atoms of oxygen differ from the atoms of every other element in the following ways:

- (a) the nuclei of oxygen atoms have a different number of protons than the nuclei of any other element;
- (b) atoms of oxygen have a higher ratio of neutrons to protons than the atoms of any other element;
- (c) neutral atoms of oxygen have a different number of electrons than neutral atoms of any other element;
- (d) atoms of oxygen have different chemical behavior than do atoms of any other element.

Answer: (b).

Problem 17

List the number and kind of fundamental particles found in a neutral lithium atom that has a nucleus with a nuclear charge three times that of a hydrogen nucleus and with approximately seven times the mass.

Answer

$$3p, 4n, 3e^-$$

Don't represent the electrons as orbiting around the nucleus. This picture is not consistent with modern quantum theory, and is not used in this course. Chapter 9 will cover the structure of atoms.

Problem 18

Helium, as found in nature, consists of two isotopes. Most of the atoms have a mass number 4, but a few have a mass number 3. For each isotope, indicate the:

- (a) atomic number ;
- (b) number of protons ;
- (c) number of neutrons ;
- (d) mass number ;
- (e) nuclear charge.

Answer

	Helium 4	Helium 3
Atomic number	2	2
Number of protons	2	2

	Helium 4	Helium 3
Number of neutrons	2	1
Mass number	4	3
Nuclear charge	2+	2+

Problem 19

On a separate sheet of paper copy and complete the following table. Do not write in this book.

Element	Atomic No.	Particles Per Atom			Mass Number		
		Protons	Electrons	Neutrons			
Aluminum (Al)	13	4			27		
Beryllium (Be)	83				9		
Bismuth (Bi)					209		
Calcium (Ca)	15	6	20	20			
Carbon (C)			6				
Fluorine (F)			15		9	16	19
Phosphorus (P)	53						127
Iodine (I)							

Answer to Problem 19

Element	Atomic No.	Particles Per Atom			Mass Number
		Protons	Electrons	Neutrons	
Aluminum (Al)	4	13	13	14	
Beryllium (Be)			4	5	
Bismuth (Bi)		83	83	126	
Calcium (Ca)	20	20			40
Carbon (C)	6		6		12
Fluorine (F)	9	9		10	31
Phosphorus (P)	53	15	15		
Iodine (I)		53		74	

Problem 20

How do isotopes of one element differ from each other?
How are they the same?

Answer

They differ in mass and in number of neutrons.
They have the same number of protons and electrons, and their chemical behavior is the same.

Problem 21

Use the exact masses and the percent abundance in Table 8-4 for Cl-35 and Cl-37 to calculate the average molar mass for atomic chlorine.

Answer

75.53% of the chlorine atoms have molar mass 34.969

24.47% have 36.966

$$\left(\frac{\text{g Cl-35}}{\text{mole Cl-35}}\right)\left(\frac{\text{mole Cl-35}}{\text{mole natural Cl}}\right) + \left(\frac{\text{g Cl-37}}{\text{mole Cl-37}}\right)\left(\frac{\text{mole Cl-37}}{\text{mole natural Cl}}\right)$$

$$(34.969)(0.7553) + (36.966)(0.2447) \\ = \text{molar mass of naturally occurring chlorine} \\ 26.4121 + 9.0456 = 35.4577 \text{ or } 35.46 \text{ g/mole}$$

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

- Chlorine monoxide gas, Cl_2O , absorbs light at frequencies near 2.0×10^{13} and 7×10^{14} cycles per second.
 - Name the spectral region in which each frequency falls.
 - Would you expect this compound to be colored? Explain.

Answer

- The first frequency is in the infrared region, the last in the visible.
 - Yes, the compound would be colored. The light in the visible region at 7×10^{14} cycles per second would be absorbed. The student is not asked to, but he may supply the information that this light is blue. Since the blue light is absorbed, the gas would appear orange.
- Prospecting for uranium minerals is aided by the use of "black-light" lamps. These lamps, which emit light of frequencies near 10^{15} cycles/second (which the human eye does not detect as visible light), cause the minerals to glow (to become "fluorescent"). In what spectral range is the light emitted by the lamp?

Answer

The frequency 10^{15} cycles/sec is in the ultra-violet region.

- Commercial heat lamps emit light of frequencies near 3×10^{14} cycles/sec. In what spectral range is this light?

Answer

This is the infrared region. It is so near the red end of the visible region that it is called the "near infrared," and heat lamps usually glow with a reddish color. Nevertheless their maximum emission is beyond the red sensitivity of the human eye.

For questions 4 and 5 consider the following data.

In an experiment, 1 mole of electrons passing through a series of solutions causes $\frac{1}{2}$ mole of one metal (X) to be deposited from a solution and $\frac{1}{3}$ mole of a different metal (Y) to be deposited from a second solution.

- Write the formula for each of the metallic ions which were reduced to form the metals X and Y.

Answer: X^{2+} and Y^{3+} .

- Explain, in terms of basic atomic structure, how it is possible for an electric current to "count" atoms.

Answer

According to the atomic theory, atoms are composed of protons (+), electrons (-), and neutrons. The positive metallic ions are atoms that have lost one or more electrons. If we assume an electric current to be the flow of electrons along a conductor, then the current is able to "count" atoms, since each metallic ion species can only accept an integral number of electrons to form a neutral metallic atom. For $1+$ ions, only one electron is needed per ion. For $2+$ ions, two electrons are required per ion, and so forth.

6. In the Millikan oil drop experiment the tiny charged droplets can be made to rise, fall, or remain stationary between the charged plates. Account for the fact that, with the plate voltage set so that at least one droplet is stationary, others may be rising or falling at different rates. The upper plate is negative. Assume all droplets to be of the same mass.

Answer

Uncharged droplets would be unaffected by the charged plates and therefore would fall. Droplets having less positive charge than the stationary droplet would also fall, while droplets having more positive charge would rise.

7. Which of the following properties differ for

Atomic Mass	Atomic Number	No. of Protons	No. of Neutrons	No. of Electrons in Neutral Atom	Positive Charge on Nucleus
12	6				
13					

Answer to Question 9

Atomic Mass	Atomic Number	No. of Protons	No. of Neutrons	No. of Electrons in Neutral Atom	Positive Charge on Nucleus
12	6	6	6	6	6
13	6	6	7	6	6

The next three problems use this information. Naturally occurring chlorine has two isotopes. Three-fourths of the atoms are ^{35}Cl and one-fourth are ^{37}Cl .

10. If a mole of $^{35}\text{Cl}\text{—}^{37}\text{Cl}$ molecules react with a mole of $^1\text{H}\text{—}^2\text{H}$, what products will form?

Answer



11. What is the mass of a mole of $^{35}\text{Cl}\text{—}^{37}\text{Cl}$ molecules?

neutral atoms of two isotopes of the same element?

- (a) atomic number
- (b) mass
- (c) number of electrons
- (d) general chemical reactions

Answer: (b).

8. What is wrong with the statement, "Atoms of element X have $8.5+$ nuclear charge"?

Answer

Nuclear charge is measured in fundamental units of charge, and occurs only in unit amounts. Fractional charges are not found.

9. Complete the following table for two naturally occurring isotopes, both of element X.

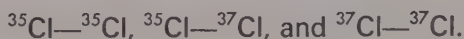
Answer to Question 11

72 g.

12. If you had a device that could separate molecules by their mass, what would you expect it to show for a sample of natural $\text{Cl}_2(\text{g})$?

Answer

Three groups, or kinds, of molecules should be seen. These would be:



Models for Atomic Structure



Intent and Approach

The approach in this chapter stems from a consideration of some of the fundamental questions raised earlier. The student is by now aware that chemical behavior is related to electrons—he has seen how both the halogens and the alkali metals tend to achieve the noble gas configuration. He has seen the regular trend in chemical properties across a row of the Periodic Table. In this chapter we attempt to “explain” these important relations.

Our intent in this chapter is threefold:

1. To provide a basis for explaining the Periodic Table (in terms of the hydrogen atom spectrum).
2. To provide a valid picture of the electron distribution of an atom, as currently accepted.
3. To provide a basis for explaining the chemical trends shown by elements and organized in the Periodic Table (in terms of ionization energy and its periodic variation).

To achieve the first of these aims, we make a tentative connection between the spectrum and ionization energy. The fact that there are lines of energy less than 313.6 kcal/mole, the ionization energy, suggests intermediate “steps” or stages. A staircase analogy is developed to

present this important concept in nonscientific language. Next the energy level diagram is shown as a scientific example of the same type. Finally, the connection between the energy levels of the hydrogen atom and the electron population of noble gases establishes these energy levels as a basis for understanding the Periodic Table.

Our second goal is to implant a valid picture of the electron distribution in an atom, displacing, if necessary, any erroneous views concerning the electron distribution that the student may have acquired. First, our space-filling models convey the impression that the atom has boundary surfaces. We are convinced it does not. Second, the student may have the erroneous view that the term “orbital” means that the electron has a planetary trajectory. Experimental evidence shows this is not correct. There is no advantage in fostering an incorrect idea.

Our third aim is achieved by detailing the connection between ionization energy and electron occupancy. This connection provides a substantial experimental basis for understanding the chemical trends across the Periodic Table—the trends expressed classically in terms of electronegativity and valence.

SCHEDULE AND RELATED MATERIAL

Suggested Time : 12 days

Text Section	Topic and Related Work	Exercises	Problems		
			Easy	Medium	Hard
9-1	<i>Film:</i> Ionization Energy				
9-2	Ionization Energy, H Spectrum	1		1-5	
9-3	Staircase Analogy	2			
9-4	The Hydrogen Atom				
9-5	Bohr's Model				
	Orbitals—Meaning		6-9		
	<i>Film:</i> The Hydrogen Atom as Viewed by Quantum Mechanics				
9-6	Orbitals—H Atom				
	Demo. 26. Models of <i>p</i> Orbitals				
9-7	Orbitals—Other Atoms		10	11-13	
9-8	Orbitals and Periodic Table			14-18	
9-9	Orbital Occupancy and Periodic Table				
9-10	Ionization and Periodic Table				
9-11	4th Row Elements	3			
9-12	Review				

Note: Experiments 23 and 24 plus Demonstration 27 can be done any time during Chapter 9.

Outline

The hydrogen atom spectrum from Chapter 8 is compared with the ionization energy. The presence of many lines of intermediate energy suggests "steps" or levels (9-1).

A nonscientific, staircase analogy is developed (9-2) and applied to the hydrogen atom spectrum (9-3) to deduce the energy levels.

Bohr's proposal gave the first explanation of the spectrum. It was developed into the quantum mechanical model (9-4).

The treatment of electron probability distribution, or orbitals, is explained (9-5) and applied to the hydrogen atom (9-6).

Atoms of all elements have orbitals, although our equations allow only approximate solutions for them. The schematic arrangement of electron levels for atoms containing many electrons is given (9-7) and used to show the arrangement of electrons in atoms (9-8).

Electron arrangements (particularly *s* and *p* orbitals) are shown to have a direct relation to periodic chemical behavior (9-9) and ionization energy (9-10).

Elements beyond argon are used to indicate briefly the use of *d* and *f* orbitals (9-11). A final section (9-12) gives a review.

New Concepts

1. Light is a form of energy. The amount of energy is related to the frequency of the light:
 $E = h\nu$.
2. Atoms can exist only in certain "stationary

states"; each state is characterized by a specific energy. Excitation places atoms in higher energy states temporarily; the emission of light (a form of energy) accompanies the

- return of the atom to a state of lower energy.
3. The location of the electron in an atom is described by orbitals characterized by quantum numbers. An "orbital" refers to a spatial distribution of the electron.
 4. Atoms have no boundary surfaces; the electron distribution extends to infinity.
 5. The ionization energy describes the amount of energy required to completely remove an electron from a gaseous atom.
 6. Ionization energy increases across a row of the Periodic Table.
 7. The successive ionization energies for a single element explain the number of valence electrons.
 8. Chemical properties of elements are related to ionization energy and electron configuration.

Development

In Chapter 7 we presented a brief survey of the organization of the Periodic Table and noted the existence of a set of noble gases. We then related the properties of the halogens and the alkali metals to the tendency of these elements to attain the electron population of one of the noble gases. "Wondering why" this tendency should be exhibited is the fundamental question this chapter attempts to explain. The explanation given is extended to cover the periodicity of properties illustrated in the Periodic Table.

A brief historical survey is given to show how new experimental evidence can force scientists to abandon commonly accepted views. Of course, we use only part of the evidence that led to the quantum mechanical revolt against classical physics. It is that part of the evidence relating to the possible energy states of an atom. Bohr is given credit for postulating "stationary states" to explain experimental data, although acceptance of his postulate meant abandoning classical laws of motion which had remained intact for over 200 years. Observe the significance of this time period. In 1900, every scientist alive was several generations removed from the period when doubt remained about these classical laws. These two centuries had seen many successes as dramatic as the predicted return of Halley's comet and witnessed the development of the mathematical elegance that has immortalized names like LaGrange and Hamilton. Newton's laws and, later, Maxwell's equations had generally become accepted as scientific dogma. In this setting, Bohr found it necessary to pro-

pose that the laws of motion for an electron interacting with a proton differ from the classical laws of motion. His argument was simple and compelling. With the classical laws of motion, the stability of the hydrogen atom, and the well-known hydrogen atom spectrum were inexplicable. Hence, Bohr accepted the observed stability of the hydrogen atom and looked for a model in accord with the hydrogen atom spectrum. His success founded quantum mechanics.

There are two important lessons here. First, we see that theories are accepted only as long as they are useful in explaining experimental facts. Second, the longer a theory is used with success, the harder it is to recognize its failings and get new theories accepted.

Film, IONIZATION ENERGY,

fits here. See p. 153 for summary.

9-1 Ionization Energy and the Hydrogen Spectrum

It may be helpful to motivate interest in this section by first recalling that the difference in the properties of alkali metals and those of the halogens was discussed in terms of the atom's tendency to acquire the electron population of a noble gas. This will raise the question of what energy change is implied by such a change in electron population. What energy effect accompanies the change when a neutral sodium atom

loses an electron? This process is called ionization, and the energy effect is called ionization energy. (Be sure the student realizes that the entire discussion refers to isolated atoms—i.e., gaseous atoms.) By studying ionization energies, perhaps we can understand why sodium loses an electron in a chemical reaction but chlorine does not.

The initial discussion of ionization energy has these objectives:

1. To indicate what "ionization energy" means.
2. To indicate how ionization energies are measured.

Later we will relate ionization energies to the energy level diagrams. The film, "Ionization Energy," is specifically designed to show the experimental methods used in measuring this important quantity.

The intent of this section is to start the deduction of the energy levels of the hydrogen atom from its spectrum as emitted from a glow discharge tube. After accepting the relation $E = h\nu$, the student has only one logical hurdle to pass. He must see how fixed increments of energy imply the energy level diagram.

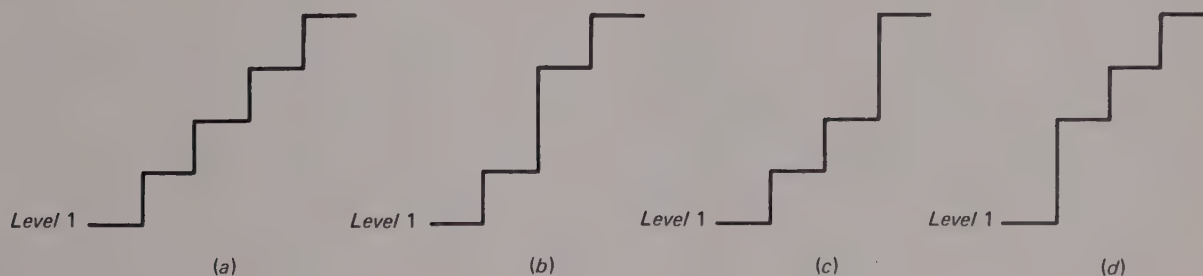
It is necessary to see how measurements of differences such as $E_2 - E_1$ can give information about E_2 and E_1 individually. Each frequency emitted reveals the difference in energy between two possible energies the atom can possess. The

systematic spacings of the lines within a group (as revealed in Exercise 9-2) suggest that these energy differences are related. We can assume, as one possible relation, that each line in a group shows an energy difference relative to the *same* state, E_1 . This possible interpretation is communicated via the staircase analogy—a familiar device with fixed incremental steps. The assumption leads to the establishment of the series of steps in Textbook Figure 9-3.

We need only find some corroborative evidence that will show that our assumption leads to a useful model. This we find by observing that the deduced staircase implies that other lines should be possible, and the other lines turn out to be precisely those observed in the visible group.

9-2 A Model That Explains the Hydrogen Spectrum

This section begins a series of sections whose goal is to have the student understand the major results of the quantum mechanical theory of the atom. The mathematics of this theory is much too advanced for the student; so these sections present the results in pictorial fashion. To begin, Section 9-2 contains a simple analogy in non-scientific terms. Make sure the class absorbs the main point: from the observed changes in level we deduce the arrangement of levels. The



Report of:

Random jumps	1, 2, 3, 4,	1, 2, 3, 4	1, 2, 3, 4,	1, 2, 3, 4
Jumps down to level 1	1, 2, 3, 4	1, 3, 4	1, 2, 4	2, 3, 4
Jumps down to level 2	1, 2, 3	2, 3	1, 3	1, 2
Jumps down to level 3	1, 2	1	2	1

FIGURE 9-1

Four staircases that give the same "random jump" spectrum but differ for jumps down to a specified level.

indivisible nature of the changes is important too. That is, there are certain levels and *no* intermediate positions.

You can help bring out and expand the point of Exercise 9-1 by the following example: Suppose the report from a group of children jumping at random on a staircase contains only changes of 1, 2, 3, or 4. Get the students to suggest the staircase has four steps each one unit high, similar to the example in the Textbook. Then ask if that is the only staircase that will fit the report. It isn't. Figure 9-1 contains others. You might supply one or more of these and ask the students to suggest a way to choose between them.

Lead them to suggest a more controlled "experiment." We might tell the children to select any level they wish, then direct them to jump down to level number one. Their reports will now differ for the various models. You can carry this on as you like. The idea of transitions to different levels is used (for the hydrogen atom spectrum) in the next section. Jumping down corresponds to the emission of energy as electrons move to lower energy levels in the atom.

9-3 The Hydrogen Atom

9-4 Bohr's Model for the Hydrogen Atom

The first of these two sections is quite short. It applies the staircase model directly to the ultraviolet spectrum of hydrogen atoms to get the energy level diagram. It should follow easily from the previous section.

Notice the connection between "level number" in the analogy and "quantum number" in the equations of Section 9-4. This connection is intentional and should be stressed. You can make the mathematical relation, $E_n = \frac{313.6}{n^2}$, furnish an opportunity for discovery by the students. Before Section 9-4 is assigned, ask them to find a connection between the energy values in Textbook Table 9-1 and the level numbers in Textbook Figure 9-4. Level number 2 is assigned to 235.2 kcal, 3 to 78.4, and so on. Even if no one finds the correct relation, it is dramatic when the simple relation is revealed. Use a systematic approach to the result in order to convince the student that a logical approach is better than trial and error. Here is a sample line of discussion.

- (a) Begin with a plot showing energy, E , versus level number. The discussion of the plot should focus on the smooth dependence

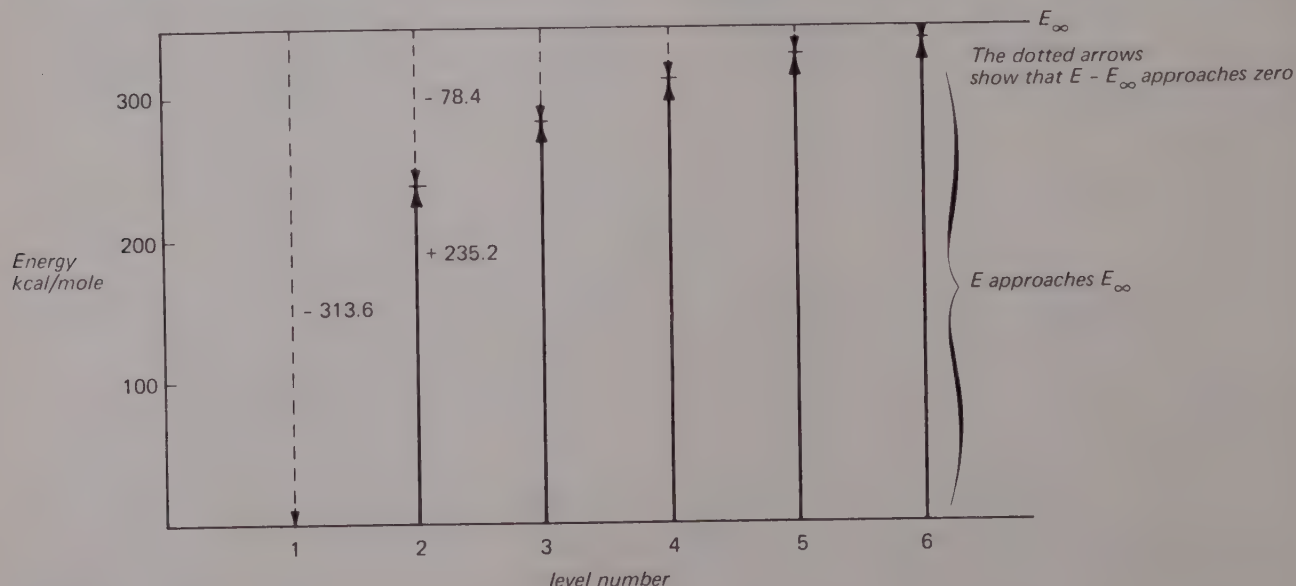


FIGURE 9-2

Energy of ultraviolet lines in the atomic hydrogen spectrum versus level number. See paragraph (a) for development of figures in the class discussion.

upon n (which encourages seeking a mathematical formulation) and on the asymptotic behavior as n becomes large (the most important clue to the mathematical relation we seek). Let class discussion lead to an estimate of E_∞ . The value, 313.6 kcal, has been given in Section 9-1, but this use will emphasize it. Use the number the class decides upon if it is within three or four kilocalories of the correct value, 313.6 kcal.

- (b) On the chalkboard, make a table of n versus E and a plot of n versus E . Add the asymptotic

value, E_∞ , for very large n ($n = \infty$). Now observe that it may be more convenient to look for a relation between n and the difference between E and E_∞ instead of between n and E itself. On the plot, this amounts to shifting attention from the solid arrows to the broken arrows. This is simpler because now we are looking for a function that approaches zero as n becomes large. Mathematically, we are changing from E to $E - E_\infty$ as our variable. Now add the third column to the table, calculating $E - E_\infty$.

Column Number	1	2	3	4	5	6
Discussed in paragraph	(a) n	(a) E	(b) $E - E_\infty$	(c) E_∞/n	(c) E_∞/n^2	(c) E_∞/n^3
	1	(0)	-313.6	-313.6	-313.6	-313.6
	2	235.2	-78.4	-156.8	-78.4	-39.2
	3	278.8	-34.8	-104.5	-34.8	-11.6
	4	294.0	-19.6	Fill in other entries as discussed in paragraph (d).		
	5	301.1	-12.5			
	6	304.9	-8.7			
	.	.	.			
	.	.	.			
	.	.	.			
	∞	313.6	(0.0)	0	0	0

- (c) We now need a function involving E_∞ and n that has the value -313.6 at $n = 1$ and approaches zero as n becomes large. Observe that if we multiply by n or some power of n , the product becomes larger as n becomes larger. On the other hand, if we divide by n or some power of n , the quotient becomes smaller as n becomes larger. Perhaps we are looking for an inverse relation between $E - E_\infty$ and n . Perhaps $E - E_\infty$ is proportional to $1/n^x$.

To see whether this is reasonable, first consider possible values of x , adding columns to the existing table as you proceed, and then demonstrate that every one of these passes through the points E_∞ (when n is taken to be 1) and 0 (when n is taken to be infinity).

- (d) Once the reasonableness of an inverse power of n is established we need only fill in enough of the last three columns to see that E_∞/n and E_∞/n^3 do not fit at all but that E_∞/n^2 fits quite closely (even if E_∞ is a few kilocalories in error). Observe that each value in column 5 or 6 is derived from the one to its left simply by dividing by integers. Thus the second entry in column 4 is

$$-\frac{313.6}{2} = -156.8$$

The second entry in column 5 is

$$-\frac{313.6}{2^2} = -\frac{313.6}{2 \cdot 2} = -\frac{156.8}{2} = -78.4$$

The second entry in column 6 is

$$-\frac{313.6}{2^3} = -\frac{78.4}{2} = -39.2$$

Thus you can readily complete the table at the chalkboard, even with an unfamiliar value for E_{∞} .

The next important point is to begin connecting the values of n , n^2 , and $2n^2$ to the electronic structure of the noble gases. Use Table 9-2 in the Textbook to show the connection *and* to remind the student that the *observed* chemical facts of inertness and nuclear charge are what spurred the construction of the quantum-mechanical model.

The section ends with six summary statements on atomic structure. Point out that the "Basis for Statement" column contains experimental facts while the "Statement" column gives the regularities derived from them.

9-5 The Meaning of Orbitals

9-6 The Orbitals for the Hydrogen Atom

The first point to make is to give meaning to the word "orbital." An orbital tells us where the electron "spends its time." The information it contains can be shown by considering the information that would be contained in an instantaneous photograph of three or four bees near a flower. We would see one set of locations of the bees but would receive little information about how the bees move about. If we take a whole succession of photographs, however, we begin to discover where the bees prefer to be in relation to the flower. Many of the photographs would show one or more bees very close to the flower; only a few of the photographs would show a bee a long distance from the center of fragrance. Taking all of the photos together, we have a probability picture of the bees around a flower. If the negatives of the photos are all superimposed, we see a distribution of dots that are quite close together near the flower and far apart away from the

flower. The density of dots at any point is proportional to the probability of finding a bee at that point.

This is exactly the meaning of "orbital" in quantum mechanics. Notice that the probability distribution of the bees is continuous and extends to infinity, but that this does not mean that the bees have been vaporized into a diffuse bee-cloud. Rather, each bee is at a point at each instant, just as each electron is at a point at each instant. This may be a good time to evoke from the class two criticisms of the Styrofoam models. The students will probably recognize that the orbitals shown in Figures 9-5 to 9-8 of the Textbook have no boundaries, whereas the models do. In addition, the Styrofoam has uniform density and suggests, incorrectly, that the electron is somehow spread out evenly over the volume. (In fact, the term "electron cloud," used by some chemists, is carefully avoided in this text because of the incorrect connotation of the word "cloud.")

Another apt and important property of the analogy is that, although the superimposition of these photographs tells us where the bees are apt to be found, it says nothing about how they get there. We know the bees have energy of motion, but we know nothing of their trajectories. This is exactly the situation we find for an orbital: quantum mechanics tells us where the electrons are (in probability terms); it assures us they have kinetic energy, but it does not reveal their trajectories. Notice, however, that the distribution clearly rules out a planetary trajectory, since a planetary trajectory rarely places an electron near the nucleus, whereas this is often a position of high probability for the electron in an atom.

Make the student aware that as n becomes larger, the electron spends more and more time far from the nucleus. This is in accord with the fact that the energy of attraction (a negative number) decreases in magnitude as n becomes larger. This leads quite naturally to the significance of $n = \infty$. The electron now spends its time at such large distances that it is no longer "attached" to the proton. In that condition the atom has an excess of positive charge in the nucleus and is said to be *ionized*.

Film, THE HYDROGEN ATOM AS VIEWED BY QUANTUM MECHANICS,

fits here. See p. 153 for summary.

The energy level diagram for hydrogen, Textbook Figure 9-9, shows the relative numbers and positions of the different kinds of orbitals. Its main purpose is to act as a stepping stone to the diagram for many-electron atoms. The latter diagram will be used extensively.

Demo. 26, MODELS OF *p* ORBITALS

fits here. See p. 118 in the Laboratory Guide.

9-7 Orbitals for Atoms with More than One Electron

At this point, the many-electron energy level diagram is needed. The hydrogen atom levels predict that the third row of the Periodic Table should have eighteen elements instead of eight. The explanation can be found in the energy level diagrams of many-electron atoms. These diagrams show that some energy levels are shifted. The shift is explained as the result of inter-electron repulsion (not present in the hydrogen atom). The principal quantum numbers are still useful, but now the *s*, *p*, *d*, *f* notation is needed to designate sublevels of differing energy. The emission spectra of many-electron atoms show just how the energy levels change. Taking these shifts into account, we find the entire Periodic Table can be "explained" with the aid of the hydrogen atom quantum designations.

Textbook Figure 9-10 gives a schematic dia-

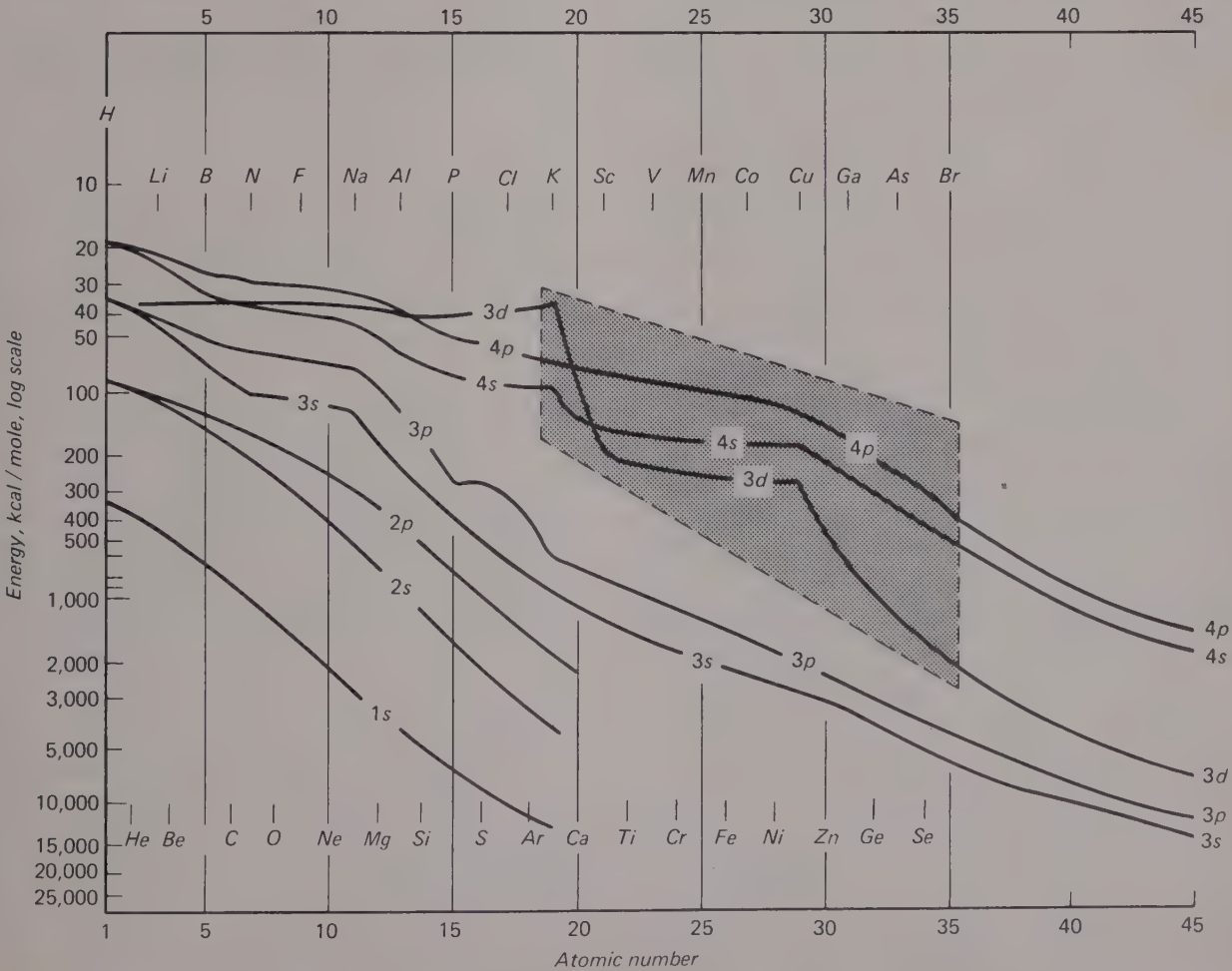


FIGURE 9-3 The effect of atomic number on the energy levels of orbitals in the first 45 elements.

gram of the energy levels. Make sure the students understand that this gives the general idea of level placement. The figure is *not exact for any particular element*. Therefore, in the figures for succeeding sections we have plotted levels in approximately correct positions for different elements. The pupil should not be surprised that a given level, say the $2s$ orbital, does not have the same energy for each element. The different sized nuclear charges attract the electrons to various degrees and the presence of more or fewer electrons causes repulsion of differing magnitudes.

Figure 9-3 shows the interesting trends in the energy level spacings of the neutral atoms as a function of atomic number. These are developed in the two supplementary references by DeVault (see *Supplementary Material*, p. 153). For example, the energy of a particular orbital increases in magnitude rapidly with increase in atomic number. For a mole of H atoms, the $3s$, $3p$, and $3d$ energy levels have the same energy, and 34.8 kcal are required to ionize a $3d$ electron. For atomic number 3 (the element lithium) the energy that a $3d$ electron would have is still about 35 kcal, but the $3s$ energy level is about 10 kcal lower, and the $3p$ energy level is about 2 kcal lower. For iron (atomic number 26) the energy of a $3d$ electron is about 275 kcal, and now the $3s$ and $3p$ energy levels are more than 1000 kcal below the $3d$ level. On the other hand, the $4s$ level has dropped down near the $3d$ level. For the higher atomic numbers, the $3d$ energy level has dropped even more, and the $3s$, $3p$, and $3d$ levels have about the same energy again. The $3d$ energy levels act as valence orbitals for atomic numbers 19 to about 30, and in this range of atomic number the energies are approximately as shown in our schematic energy level diagram.

9-8 Orbitals and the Periodic Table

The crucial aspect of this section is to develop empirically the need for the Pauli Principle. For the purposes of this course, the operative principle is: *one or two electrons, but never more than two, can occupy the same orbital*. This

empiricism springs from our attempts to relate the numbers of hydrogen atom orbitals to the number of elements per row of the Periodic Table. We observe in the Periodic Table the row lengths 2, 8, 8, 18, 18, and 32. We observe for the hydrogen atom the numbers of orbitals $1^2 = 1$, $2^2 = 4$, $3^2 = 9$, $4^2 = 16$. Moreover, we find that these numbers, multiplied by 2, give the same numbers found in the Periodic Table. For the first eleven elements, we demonstrate how the postulation of two electrons per orbital can "explain" the first two rows of the Periodic Table. As an aside, it may be noted that all of the evidence for the Pauli Principle is empirical, just as represented here. Quantum mechanics does not imply the Pauli Principle.

Some important symbolism is developed in this section. By your use, show that it is convenient and meaningful. The two ways of showing electron configurations will be used throughout the remainder of the course.

9-9 Electron Configuration and the Periodic Table

Regularities in the arrangements of electrons can now be related to regularities found in chemical behavior (Chapter 7). Use this section to pull the class together in their understanding of the configurations and their use.

9-10 Ionization Energy and the Periodic Table

The importance of ionization energies to a chemist comes from their connection to the chemical trends across a row of the Periodic Table. In Textbook Figure 9-16, the sawtooth trend in ionization energy clearly defines the periodicity in the Periodic Table. It explains that the energy needed to remove an electron from an element increases from left to right across a row but suddenly drops at the beginning of a new row. Most important, it explains, in terms of energy effects, why the valence electrons (those in the outermost, partially filled orbitals) determine the properties of the atom. The energy necessary to disturb the inner electrons is prohibitively high.

9-11 The Fourth Row of the Periodic Table

The chapter concludes with a brief discussion of *d* and *f* orbitals. The intent is to indicate they are not fundamentally different from *s* and *p*

orbitals. Do not go into their complex shapes and bonding arrangements. Some of this material will be taken up in Chapter 20.

9-12 Review**Supplementary Material****Articles**

1. D. DeVault, "A method of teaching the electronic structure of the atom, I," *J. Chem. Education*, **21**, 526 (1944).^{*} Excellent for both the advanced student and the teacher. Treats stationary states, electron distribution, Periodic Table.
2. D. DeVault, "A method of teaching the electronic structure of the atom, II, advanced topics," *J. Chem. Education*, **21**, 575 (1944).^{*} Excellent for the teacher, but may confuse students. Treats the variation of energy level spacing with increase in nuclear charge.

^{*} Included in "Supplementary Readings for Chemical Bond Approach," Chemical Education Publishing Company, Easton, Pa., 1960; reprints published by *J. Chem. Education*.

Books

1. M. J. Sienko and R. A. Plane, *CHEMISTRY*, 3rd ed., McGraw-Hill, New York (1966), pp. 46–75. Suitable for the advanced student; useful for the teacher. Treats ionization energy, electron affinity, Periodic Table.
2. H. H. Sisler, C. A. Vander Werf, and A. W. Davidson, *COLLEGE CHEMISTRY—A SYSTEMATIC APPROACH*, Macmillan, New York (1967). Suitable for the advanced student, useful for the teacher. The Periodic Table is considered in terms of energy levels, ionization energies, and chemical properties.
3. G. M. Barrow, *PHYSICAL CHEMISTRY*, McGraw-Hill, New York, 2nd ed. (1966), pp. 186–201. Provides background in depth for the teacher; too mathematical for students. Covers the Schroedinger equation, shows explicit forms of hydrogen atom orbitals, and discusses the probability distribution.

Films

For ordering information see the *List of Film Sources* at the back of the Teacher's Guide.

IONIZATION ENERGY

A CHEM Study film

Running Time: 22 minutes

This film was produced with the collaboration of Professor Bruce H. Mahan of the University of California at Berkeley. The film provides strong support of the text by showing how ionization energies are measured. Both photoionization and electron bombardment methods are demonstrated and explained. The photoionization method is demonstrated using gaseous sodium. The electron bombardment method is shown to give the same value for sodium and is then applied to the noble gases. The sawtooth periodicity of ionization energy is also developed.

THE HYDROGEN ATOM AS VIEWED BY QUANTUM MECHANICS (Advanced Version)

A CHEM Study film

Running Time: 20 minutes

Professor G. C. Pimentel of the University of California, Berkeley, collaborated on this film, which begins with an experimental arc spectrum of the hydrogen atom. The student is reminded that the success of the quantum-mechanical model in explaining this pattern of lines gives us confidence in a concept derived from the model—the orbital. The main purpose of this film is to show the present meaning of the term orbital. This is done via a simple but valid analogy—a hummingbird collecting nectar from flowers near its nest. A map of the flowers visited by the bird is used to develop four important ideas about atoms: (1) quantum mechanics speaks in terms of probability; (2) it gives only an average picture of electron position; (3) the electron is most likely to be near the nucleus, but it can be anywhere; and (4) the trajectory of the electron is not known.

Background Discussion

This chapter shows how our modern understanding of the hydrogen atom, through quan-

tum mechanics, explains the Periodic Table and the chemical trends it correlates. Unfortunately,

even experienced teachers may feel their own background is weak in this area.

With the expectation that many teachers will wish to supplement their existing knowledge, we present here a rather lengthy background discussion. It goes well beyond the needs of classroom discussion and provides, we hope, some understanding of the advantages that lie in abandoning certain traditional treatments in favor of currently accepted views.

Light and Matter: Waves or Particles?

Some properties of light are best described in terms of the properties of waves. Other properties of light are best described in terms of particles of light. The same sort of ambiguity in description applies to matter. This wave-particle duality is an essential facet of the modern setting of the physical sciences. In this course, the duality confronts us in our consideration of the properties of light and, again, in our consideration of the quantum-mechanical picture of the atom. Hence we feel that a review of some of the experimental evidence that gives rise to these alternate descriptions—waves or particles—is appropriate.

The Wave Nature of Light and Matter

Geometrical optics deals with the reflection and refraction of light. Precise mathematical description of these can be framed by attributing to light the spatial extension, continuity, and periodic variations of a wave. The description gives detailed explanations of diffraction effects in terms of constructive and destructive summations of waves. The wave view of light is, on the one hand, accurate in that it fits many experimental facts and, on the other hand, appealing in that it provides an intuitive grasp of "what is going on."

Wavelike properties of fundamental particles are now well recognized, too. Diffraction phenomena just like those observed with light have been demonstrated for fundamental particles such as electrons and neutrons. In fact the de-

duction of crystal structures through neutron diffraction is now an active field. The diffraction patterns can be interpreted in terms of wave phenomena provided the particle is assigned a wavelength fixed by its mass and velocity:

$$\lambda(\text{cm}) = h/mv \quad (1)$$

This wavelength is called the de Broglie (pronounced *de broll-ye*) wavelength.

Expression (1) can be nonrigorously deduced in this way; a light wave of frequency ν has energy $E = h\nu$. But frequency is just the velocity of light divided by wavelength, $\nu = c/\lambda$, thus $E = hc/\lambda$. Einstein related energy and mass in his equation $E = mc^2$, which by substitution gives $\lambda = h/mc$. This is identical in form with expression (1) if we recognize that the photon travels with velocity c , whereas the particle travels with velocity v .

The wave nature of matter is most firmly attested, however, by the success of quantum mechanics. The mathematics of quantum mechanics is based upon a modification of the mathematics of classical mechanics. The total energy is written as the sum of the kinetic and potential energies of the fundamental particles, using point positions and momenta as the variables. Then wherever momentum appears, a substitution is made that alters the mathematical character of the equation.* First, the equation takes on the general form of an equation describing waves. Second, it acquires a statistical character, expressing the information it contains in terms of probabilities and averages. More will be said later about the nature of the solutions to quantum-mechanical equations, but for the purposes of this paragraph, we can conclude that the well-deserved confidence given to quantum mechanics carries an implicit acceptance of the wave description of fundamental particles.

* The equation then becomes the celebrated Schrodinger equation. It is obtained by substituting a second derivative wherever momentum appears. Such a change implies that the equation becomes a second-order differential equation. If more than one dimension is involved, it is a partial differential equation.

The Particulate Nature of Light and Matter

There is no need to argue further in favor of the particulate nature of matter. Chemistry is firmly based on the atomic theory.

Light, too, has properties best treated in terms of a particulate view. Planck was the first to use this view to explain the frequency distribution of the energy radiated by a black body. He found it impossible to devise an experimental model that would fit the experimental facts until he assumed what was then a strange model. He pictured a collection of oscillators, each capable of radiating only a single frequency, and he added that the radiation process released energy in "portions" or "quanta." The energy a given oscillator released per "quantum" was assumed to be fixed by the frequency according to the now-famous relation, $E = h\nu$. The constant h is the same for all frequencies. Planck proposed this model, despite its strangeness, because the experimental facts demanded it.

Another experiment that displays the particulate nature of light, the photoelectric effect, is more easily grasped. When light of frequency ν falls on a metal surface, and the frequency is slowly increased while suitable measurements are made, one discovers that above a critical frequency, ν_0 , electrons are ejected from the metal surface. Below this frequency, no electrons are ejected, no matter how long the metal is illuminated. At frequencies above ν_0 , the energies of the ejected electrons can be measured. Changing the intensity of the light changes the number of electrons ejected per second, but not their energies. This behavior is understood in terms of the quantum view of light. Light is considered to be made up of "packages" of energy, $E = h\nu$. As ν is increased, the energy per package increases. Finally, a frequency of ν_s is reached at which the photon package of energy is sufficient to wrench an electron out of the metal surface. At still higher frequencies, the photon contains even more energy, and hence the electron is wrenched out of the metal surface, and the excess

energy appears as kinetic energy. A very simple relation between kinetic energy and frequency is observed experimentally and is predicted by this model:

$$\text{K.E.} = h\nu - h\nu_0 \quad (\nu > \nu_0)$$

Changing the intensity of the light merely increases the number of photons in the beam, but does not affect the energy per photon.

Finally, we must mention that interpretations of spectroscopic studies almost always require the Planck relation, implying the particulate nature of light. Hence, every successful interpretation of the absorption or emission of light by a molecule or an atom confirms the view that light comes in packages called photons.

Classical Mechanics and the Hydrogen Atom

Inevitably, the deduction of the nuclear atom led, within classical mechanics, to a satellite, or planetary, model of the hydrogen atom. This model seems to provide a mechanical basis for the stability of the atom. The electron is pictured as a frictionless planet circling a proton sun and held by the attractive electrostatic force between the two charged particles.

Unfortunately this model contains a false premise. Such a planetary system cannot be considered frictionless, because the two bodies possess electric charge. According to classical electrodynamics, an accelerated charge radiates light, losing energy. A circling electron is continuously accelerated as it moves in a curved trajectory. Hence an electron circling a proton in a hydrogen atom should radiate energy continuously. This loss of energy would slow the electron, reduce the angular velocity, and cause the electron to spiral toward the nucleus. Thus the theoretical scientist of 1910 could predict that nuclear atoms should collapse. He could even calculate that this collapse would occur in a small fraction of a second, shortly after atoms started behaving according to the well-established

laws of physics that govern the behavior of macroscopic bodies. Fortunately for the universe, atoms have stubbornly refused to behave according to these laws.

The Bohr Atom

Bohr first built into a useful theory the obvious experimental fact that the nuclear hydrogen atom does not collapse. He proposed that the electron in the hydrogen atom can possess only certain angular momenta—integral multiples of $h/2\pi$. Bohr "forbade" the electron to radiate by confining its angular momentum to one of a set of discrete and separated values. This model was chosen because, with only this one arbitrary change, the classical calculation of orbital motion led to the experimentally observed energy levels of the hydrogen atom. A dozen years later, the de Broglie wave picture of matter was proposed. Then it was realized that Bohr's rule corresponded to periodic electron movement in orbits, such that the distance traveled in each orbit is equal to a whole number of de Broglie wavelengths.

The Bohr model of the hydrogen atom filled two important and, possibly, essential roles. First, it introduced the idea of stationary states—an idea that set the stage for the development of modern quantum mechanics. Second, it provided a bridge between the classical planetary model of the atom and the modern quantum-mechanical model. The Bohr model, together with the de Broglie wavelength, furnished an intuitively acceptable evolutionary step in the development of the theory of the atom. Scientists who had learned to think of the atom in terms of a planetary model found it helpful to retain as much of the planetary model as the facts would tolerate.

Successes of the Bohr Atom

We can enumerate two successes of the Bohr model of the atom, one of which was immediately apparent, the other of which is important in retrospect.

1. The Bohr model reproduced exactly the energy levels of the hydrogen atom, hence it ex-

plained the till-then mysterious line spectrum of the hydrogen atom. This furnished great impetus to the ultimate development of quantum mechanics, because the simple but totally unexplained numerical relationships among the hydrogen atom frequencies had haunted physicists for almost three decades. For the first time, an explanation seemed imminent.

2. The Bohr model formulated explicitly the concept of "stationary states." At the time, this could not be counted a success; it was merely an unfamiliar premise apparently required by the experimental facts. In retrospect, we see this as one of the crucial steps toward the break with the classical laws of motion in the treatment of fundamental particles.

Failures of the Bohr Atom

The failures of the Bohr atom are more numerous than successes, though they have become apparent only slowly as the atomic theory has evolved. We can now say that the Bohr atom gives a simple physical picture of the atom, but one that is qualitatively incorrect.*

1. The Bohr atom uses a planetary model of the atom involving circular or elliptical trajectories. Quantum mechanics and experiments both show that the electron does *not* move in such trajectories. It is true that quantum mechanics remains noncommittal concerning the electron trajectory, but it does indicate the average spatial distribution of electron positions. This spatial distribution is incompatible with the Bohr trajectories. The most obvious difference is that *s* orbitals place the electron near the nucleus with high probability. There is ample experimental evidence proving that quantum mechanics is correct in

* Some of the failures listed for the Bohr atom are based upon its discordance with results drawn from quantum mechanics. This is well justified, since quantum mechanics has proven to be in accord with every atomic property for which mathematical tractability has permitted a meaningful calculation. This statement applies to many-electron atoms and molecules as well as to the hydrogen atom.

this regard. Two phenomena giving data on this point are electron-capture by the nucleus (a kind of nuclear transmutation) and the interactions between two nuclear spins displayed in nuclear magnetic resonance spectra. Each phenomenon is understandable provided the electrons spend a considerable time near the nucleus, as predicted by quantum mechanics and denied by the Bohr trajectories.

It is sometimes noted that Bohr arbitrarily "threw away" the trajectories with zero angular momentum and that these discarded orbits *do* pass through the nucleus. The inclusion of these trajectories solves one problem only to raise another. The Bohr atom fits the hydrogen atom energy levels *without* the zero angular momentum trajectories. Adding a new set of energy levels detracts from the only real success of the model.

- 2. The calculational scheme chosen to explain the energy levels of the one-electron, or hydrogen-like, atom failed to explain the energy levels of any other atom.
- 3. The Bohr model of the atom gives no clue to the origin of chemical bonding.
- 4. The basic Bohr assumption concerning angular momentum of the electron is not correct, even though it does lead to the correct hydrogen atom energy levels. Whereas Bohr assumed angular momentum equal to $n(h/2\pi)$, in which $n = 1, 2, 3, \dots$, quantum mechanics shows it to be $\sqrt{l(l+1)}(h/2\pi)$, in which $l = 0, 1, 2, \dots$. The results are compared in Table 9-1.

TABLE 9-1

Comparison of Bohr's Assumed Angular Momenta with Calculated Quantum-mechanical Averages for the Hydrogen Atom (in units of $h/2\pi$)

Quantum Number		Angular Momentum	
Bohr	QM	Bohr	QM
$n = 1$	$l = 0$	1	0
$n = 2$	$l = 1$	2	1.41
$n = 3$	$l = 2$	3	2.45
$n = 4$	$l = 3$	4	3.46

- 5. The Bohr atom provides no basis for understanding either quantization or the failure of the orbiting electron to radiate its energy. Both are simply assumed.

The Persistence of the Bohr Model

It is not surprising that the part classical, part quantum-mechanical Bohr atom strongly influenced the popular conception of the atom during the developmental period of quantum mechanics. The Schroedinger wave equation was proposed in 1926 and was developed through research done during the 1930's. Most scientists (certainly most chemists) found it convenient to adopt the Bohr atom during this period of trial as a "step in the right direction" while waiting to see what success and impact the more abstract wave mechanics would have. This permitted them to benefit from recognition of the quantization of atomic properties without abandoning their intuitively satisfying planetary view of the atom.

What is surprising is the retention of emphasis on the Bohr atom now, almost three decades after it became clear that the planetary model is not a correct picture of the atom. This can hardly be argued to be beneficial to the novice in chemistry as a bridge between his planetary view of the atom and a more correct view. *The novice has no prior basis for believing that the atom is planetary.* We cannot justify presenting the Bohr atom as a "natural" introduction to quantization, for the planetary model does not "naturally" include quantization; such an approach requires that quantization be imposed as a necessary element foreign to the model. Nor can the Bohr model be supported on the grounds that it successfully explains the hydrogen atom spectrum when it conflicts with correct predictions of another theory that also explains the hydrogen atom spectrum.

To be sure, there remains the benefit of the "case history" approach. This example offers a classic opportunity to display the path of scientific progress. Nevertheless, a very large fraction of the value is lost if the example must be presented without the mathematical detail, begin-

$$\psi = A \sin \frac{2\pi x}{\lambda}$$

The wavelength is λ , A is a constant and x the distance from the origin in the x direction. The symbol ψ , *psi*, is the amplitude. While it contains all the information available from the model we are using, it does not correspond directly to a physical quantity. We shall see later that ψ^2 tells us something about the probability of finding an electron in a given region of space.

A more general equation for a wave would contain a cosine term. It is omitted here because it will not fit the boundary requirements we will eventually put on the problem and will drop out then. From equation (1) we have

$$\lambda = h/mv$$

but mv is also momentum, p , so

$$\lambda = h/p$$

and the wave equation becomes

$$\psi = A \sin \frac{2\pi px}{h} \quad (2)$$

Equation (2) describes wave motion and involves momentum. If it is to be applied to an atom, we must be sure that it includes the idea of energy conservation. The classical laws of motion are based on the concept,

kinetic energy + potential energy = total energy

Rewriting in symbols gives

$$\text{K.E.} + \text{P.E.} = E$$

For K.E. we could substitute $\frac{1}{2}mv^2$ but since our wave equation is in terms of p it is useful to express K.E. that way too.

$$\text{K.E.} = \frac{mv^2}{2} = \frac{m^2 v^2}{2m} = p^2/2m$$

Substituting and using V for potential energy gives

$$E = \frac{p^2}{2m} + V \quad (3)$$

Multiplying (3) by ψ will not change the equality

$$E\psi = \frac{p^2}{2m}\psi + V\psi \quad (4)$$

In effect, this combines the wave description of equation (2) with the energy conservation description of equation (3). To complete the change into the quantum-mechanical form we need to replace p^2 by its equivalent from the wave expression (2). The following has been found empirically to be a workable and meaningful solution.

We cannot solve (2) directly for p but note what happens if we differentiate. Remember

$$\frac{d}{dx} (\sin ux) = u(\cos ux)$$

$$\frac{d\psi}{dx} = \frac{2\pi p}{h} \left[A \cos \frac{2\pi px}{h} \right]$$

A second differentiation leads to some simplification. Note:

$$\frac{d}{dx} (\cos ux) = -u(\sin ux)$$

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi^2 p^2}{h^2} \left[A \sin \frac{2\pi px}{h} \right] = \frac{-4\pi^2 p^2 \psi}{h^2}$$

Solving for $p^2\psi$

$$p^2\psi = \frac{-h^2}{4\pi^2} \frac{\partial^2 \psi}{\partial x^2}$$

Putting this into (4) gives

$$E\psi = \frac{1}{2m} \left(\frac{-h^2}{4\pi^2} \frac{\partial^2 \psi}{\partial x^2} \right) + V\psi \quad (5)$$

Comparison with (4) shows that requiring the equation to include the notion that energy is conserved has effected a substitution. Where we had p^2 in (4) we now have the term

$$\frac{-h^2}{4\pi^2} \frac{\partial^2}{\partial x^2}$$

The first part is a constant and the second, $\frac{\partial^2}{\partial x^2}$, is called an *operator*. An operator is just an instruction to perform an operation. This one is really not much different from the ones you already know: $+$, $\times$, $\div$, $-$. This operator instructs you to differentiate twice.

Equation (5) provides a general basis for formulating the Schrodinger equation *via* a simple, three-step recipe. First write the classical expression for the total energy; and, wherever momentum appears, substitute a derivative (times a constant). Second, leave the potential energy unchanged. Third, multiply both sides of the equation by the wave function, ψ .

As an example, let's obtain the Schrodinger equation for the hydrogen atom by this recipe. The kinetic energy term according to classical laws of motion is

$$\text{K.E.} = \frac{m}{2} (v_x^2 + v_y^2 + v_z^2)$$

The potential energy term according to Coulomb's Law is

$$\text{P.E.} = \frac{(\text{charge of electron})(\text{charge of proton})}{\text{distance from electron to proton}}$$

To make the problem easier, imagine the proton is at the origin of our coordinate system. Also, make the change to momentum as before. See equation (3). We get

$$\text{K.E.} = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2)$$

$$\text{P.E.} = -e^2 / \sqrt{x^2 + y^2 + z^2}$$

Combining these gives

$$E = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) - e^2 / \sqrt{x^2 + y^2 + z^2} \quad (6a)$$

Now applying the three-step recipe gives

$$E\psi = \frac{-h^2}{8\pi^2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) - \left(\frac{e^2}{\sqrt{x^2 + y^2 + z^2}} \right) \psi \quad (6b)$$

This equation relates the total energy (E) of the system (an electron and a proton) to the positions of the parts, their masses, and charges.

Solution of the Schrodinger Equation

Again, we begin with the case for a single dimension. To get a specific example, we define

some potential field within which the particle is moving. A very simple field will serve and have the virtue of easy solution. For x less than zero the potential is infinite. That means the particle would have to acquire infinite energy to get into that region. From the zero position on the x axis to a distance L , the potential is zero. That is, there is no opposition to the particle being there. Then beyond L , the field is again infinite. The particle is said to be confined in a square-well potential; or a one-dimensional box.

By standard methods of treating differential equations, a solution to (5) is

$$\psi = A \sin \frac{2\pi px}{h} + B \cos \frac{2\pi px}{h}$$

To show that this is a solution, differentiate twice and substitute into (5). You will obtain equation (3) showing that the ψ given is a proper one.

But in this potential field, $V = 0$ so from equation (3)

$$E = p^2/2m \quad \text{thus} \quad p = \sqrt{2mE}$$

Returning this value to the solution value of ψ gives

$$\psi = A \sin \frac{2\pi x}{h} \sqrt{2mE} + B \cos \frac{2\pi x}{h} \sqrt{2mE} \quad (7)$$

So far we have not limited the solutions of equation (7) to any particular values of ψ . At this point we add the boundary conditions. That is, we force the wave equation to give the correct amplitude values at the edges of the box. Said another way, since the amplitude of the wave is zero outside of the region from 0 to L , we must make the amplitude be zero at the boundaries.

$$\psi = 0, \quad \text{at } x = 0 \text{ and at } x = L$$

This is a reasonable sounding statement which requires some complicated mathematics to prove. It has been done and we shall proceed without the details. When $x = 0$ and $\psi = 0$ equation (7) becomes

$$0 = A \sin 0 + B \cos 0$$

The cosine of 0° is 1. However, the term $B \cos 0$ must be zero, otherwise ψ will not fit the boundary

BACKGROUND DISCUSSION

values of zero. Thus B is zero and the cosine term drops out. Equation (7) reduces to

$$\psi = A \sin \frac{2\pi x}{h} \sqrt{2mE} \quad (8)$$

which is still a solution to equation (5).

Now at the other extreme of the zero potential region, $x = L$ and $\psi = 0$.

$$0 = A \sin \frac{2\pi L}{h} \sqrt{2mE}$$

For the sine term to be zero and this statement to be true, the angle must be $0, 180, \dots, n\pi$ degrees. Thus we can say

$$\frac{2\pi L}{h} \sqrt{2mE} = n\pi \quad (9)$$

This equation is the step in which a quantum number, n , is introduced. Only certain values of n are allowed. It must be an integer. It could be positive or negative. But the two sets give the same values of ψ so only one is needed. The positive integers are used. It cannot be zero because that value would make ψ zero everywhere within the box and imply that the particle is not in that region. Yet the potential field forces it to be somewhere in the box.

Dividing (9) by L gives

$$\frac{2\pi}{h} \sqrt{2mE} = \frac{n\pi}{L}$$

and substitution in (8) gives the acceptable ψ values (usually called *eigenfunctions*).

$$\psi_n = A \sin \frac{n\pi x}{L} \quad n = 1, 2, 3, \dots \quad (10)$$

By substituting (10) into (8), we find the energy values (*eigenvalues*) are

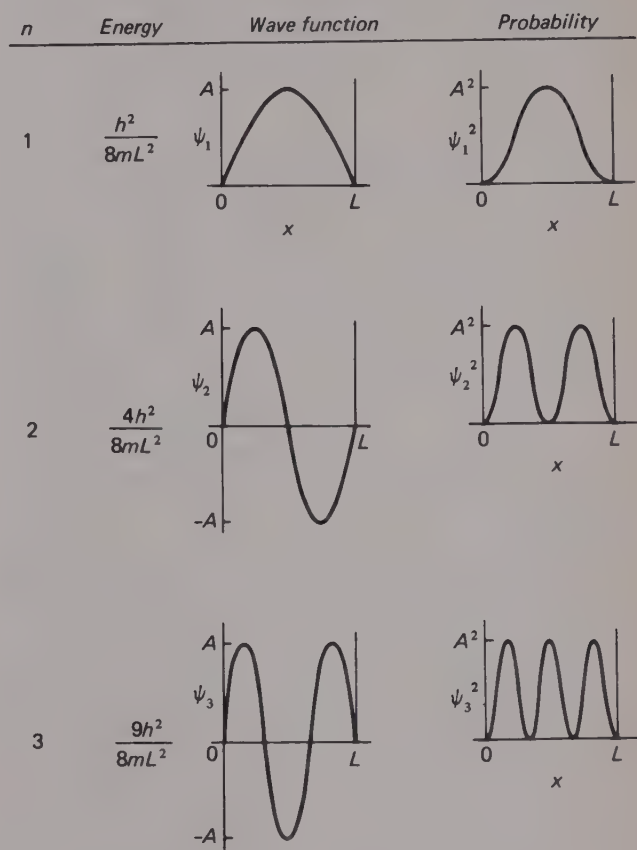
$$E_n = \frac{n^2 h^2}{8mL^2} \quad n = 1, 2, 3, \dots$$

It is one of the axioms of quantum mechanics that ψ^2 for a particular point is the probability of finding a particle at that point. It is easy to see that ψ cannot be the probability since it is often negative in some regions of space. Since the

probability of the particle being someplace in the box must be one, we can find the value of A for equation (8).

$$\int_0^L \psi_n^2 dx = 1 = A^2 \int_0^L \sin^2 \frac{n\pi x}{L} dx$$

The result is $A = \sqrt{\frac{2}{L}}$ for this one-dimensional case. We can now solve for the various eigenfunctions and the first three, along with the plots of ψ^2 , are displayed below.



The figures on the left are representations of the wave functions. To the right are probability distributions. These correspond to the one-dimensional orbitals for this particle. When the particle is in the lowest energy level, E_1 , the particle is likely to be found at the center of the region $0 \leq x \leq L$. In the second energy level,

it may not be found there at all. Rather it is most frequently near $x = 1/4$ or $3/4$.

The Hydrogen Atom

The same general line of reasoning, applied to three dimensions, allows solution of the usual form of Schrodinger's equation. As the potential field must be limited in three dimensions, three quantum numbers are introduced. They are written n , l , and m .

The worst is over. Now we can compare the classical equation (6a) to the quantum-mechanical equation (6b). First we note that the potential energy term, $-e^2/\sqrt{x^2 + y^2 + z^2}$, is present in both equations. This term tells us that the electron-proton electrostatic interaction is no different in the quantum-mechanical atom than it was in the classical atom. Specifically, the electron has not been vaporized into a charge cloud. The contribution to the potential energy at any instant is like that of a point electron interacting with a point proton separated by some definite distance, $r = \sqrt{x^2 + y^2 + z^2}$. This shows that the terms "electron cloud" and "charge cloud" can be unfortunate and misleading. A more apt expression is "probability distribution."*

Next we focus our attention on the function ψ . This function is chosen so as to satisfy equation (6b). Mathematical analysis shows that there is not just one but a set of solutions $\psi_1, \psi_2, \psi_3, \dots$, and each solution satisfies equation (6b), provided we substitute the correct one of a set of numerical values of the energy parameter, $E_1, E_2, E_3, \dots$. To each solution ψ_1 there is one and only one mathematically acceptable value of the energy, E_1 . The Schrodinger equation (6b) interests us because the acceptable values of E are the exact energy levels of the hydrogen atom.

By solving equation (6b), then, we learn the possible energy levels from the values of E . All other information about the atom is contained in ψ . This function, called the wave function,

* Even our space-filling models of an atom can be misinterpreted as suggesting (incorrectly) that the electron is everywhere in the atom at once.

tells us only averages and probabilities. It tells us the probability that the electron will be found at a particular point, but not how it would get there (its trajectory) nor how long it will remain nearby (its velocity passing through the point). That is, ψ contains the information that would be contained in a time exposure of an atom. From this time exposure we can tell where the electron spends lots of time, where it spends little time, its average kinetic energy, average momentum, average dipole moment, etc. Yet such a time average is completely noncommittal as regards instantaneous properties. It gives us no information about instantaneous movement of the electron. We can postulate, if we wish, that the electron has a trajectory—it has an average kinetic energy—but if we do, it must be a trajectory whose average agrees with the known time average. (This requirement spells out the complete unsuitability of the Bohr trajectories.) But quantum mechanics does not imply there is a trajectory. Indeed, it places limitations on what we can know about the electron movement through the Uncertainty Principle. As regards quantum mechanics (and ψ) there is no need to discuss the electron trajectory in the atom, since, as far as we know, it cannot be detected.

Thus the wave function, ψ , describes the probability distribution of the electron in space.* Such a probability distribution is called an *orbital*.

The Nature of a Quantum-mechanical Orbital

The evolution of thinking with regard to a particular physical phenomenon is sometimes told in its terminology. This is so for atomic structure. The energy levels of the hydrogen atom, for example, are designated s, p, d, f , etc. These letters are not now considered as abbreviations, but once they were. The symbols originally classified an atomic spectral line in accordance with its appearance in a spectral

* More accurately, $\psi^2 dV$ gives the probability of finding the electron in a volume element dV , provided ψ has been "normalized"—multiplied by a constant so that the total probability over the entire space is unity: $\int \psi^2 dV = 1$.

BACKGROUND DISCUSSION

photograph: *s* meant "sharp," and *d* meant "diffuse." The symbol *p* meant "principal," reflecting the then current belief that these lines had a special significance. When the Bohr atom was proposed, it became clear that the lines corresponded to transitions between two energy states of the atom. Connections between the spectral lines and the hydrogen atom energy levels led to a natural transfer of these symbols to the Bohr energy levels.*

At this time, the planetary model of the atom placed an indelible imprint on atomic nomenclature. The electron trajectory of the Bohr atom was, quite naturally, called an orbit.

As quantum mechanics evolved, the function ψ supplanted the Bohr trajectory as our statement of what is known about the position of the electron. The term orbital was transferred to the probability distribution defined by ψ . The etymological unsuitability of the term is more of a detriment than is that of the symbols *s*, *p*, and *d*, however. The word orbital directly suggests a type of electron motion that conflicts with the true meaning of ψ .

Actually, ψ predicts time averages of atomic properties—the average electron momentum, the average electron kinetic energy, the average electron-proton distance, the average angular momentum. In addition, it gives probability information on the instantaneous electron position. For example, it predicts that if many separate experiments are performed to locate the electron in a hydrogen atom, 90% of the experiments will find it at a point closer than 1.42 Å from the proton. Moreover, 90% of the experiments will find the electron farther than 0.29 Å from the proton. The radius at which the electron is most likely to be found is 0.53 Å (the radius of the first Bohr orbit!), but there is a 2% probability that the electron will be either as close as 0.1 Å or as far from the proton as 2.24 Å.

The wave function ψ does *not* tell us that the electron will surely be at a particular point at any particular time. Neither does it insist that

the electron moves from point to adjacent point in a systematic trajectory. It simply makes no statement about trajectory. What, then, should be said about trajectory? Probably it is best to de-emphasize it, laying stress instead upon the fact that quantum mechanics tells us in terms of probability how the electron occupies the space around the proton. There is no question that probability distribution is a concept of deep significance in quantum mechanics. It remains to be seen whether the notion of trajectory is really needed on the atomic scale. It is even conceivable that the notion of trajectory is merely an anachronism that persists while we get used to thinking about quantum-mechanical counterparts of kinetic energy and angular momentum without it.

The function ψ is called the wave function. Its square fixes the spatial probability distribution that is called an orbital. This function is identified by integer numbers called quantum numbers. Each possible set of quantum numbers defines a probability distribution, hence an orbital.

The Significance of Hydrogen Atom Quantum Numbers

The hydrogen atom wave functions are identified by four quantum numbers, *n*, *l*, *m*, and *s*. The first three come from imposing boundary conditions as discussed previously. The fourth, *s*, is introduced to account for the behavior of electrons in magnetic fields. The table shows the names, values, and general meaning of the numbers.

An orbital is completely fixed when *n*, *l*, and *m* are specified. According to the Pauli Principle, only two electrons can occupy the same orbital. We can now add that these two electrons must have different values of *s*. Hence the Pauli Principle can be restated in the form: "No two electrons can have the same values of all four quantum numbers *n*, *l*, *m*, and *s*."

Some students may wonder why it should be that the complicated probability distributions can be characterized so simply by integers. An appropriate and meaningful model can be based upon a vibrating string fixed at both ends. At

* Higher orbitals are designated *f* (fundamental), *g*, *h*... in alphabetical order. The letter *e* was skipped because of its other uses as a symbol.

Summary of Quantum Numbers

Symbol	Name	Values	Meaning
n	principle	$1, 2, 3, \dots, n$	fixes size of orbital and value of energy. Larger n means greater average distance of electron from nucleus and higher (more positive) energy.
l	angular momentum	$0, 1, 2, \dots, n - 1$	fixes shape of orbital $l = 0$ spherical s orbital $= 1$ two-lobed p orbital $= 2$ four-lobed d orbital $= 3$ more complex f orbital
m	magnetic	$-l, \dots, 0, \dots, +l$	defines orientation of orbitals in a magnetic field.
s	spin	$-\frac{1}{2}, +\frac{1}{2}$	defines orientation of electron in a magnetic field.

low vibration frequencies, there is one loop, or antinode. As the vibration frequency is raised, a node appears at the center, and two antinodes appear. At successively higher frequencies, three, then four, antinodes appear. The most natural way of differentiating these vibrational motions consists in representing, by an integer, the number of nodes or antinodes. The integer is analogous to a quantum number.

This is the significance of the integral values taken on by n , the principal quantum number, which tells the number of nodal surfaces—surfaces at which the probability of finding the electron becomes zero. For $n = 1$ there is but one nodal surface, and that surface is at infinity. Every orbital includes this node at infinity. For $n = 2$ there are two nodal surfaces, one in addition to the node at infinity. The $2s$ orbital has spherical symmetry, but there is a finite value of r at which the probability becomes zero. For hydrogen this is $r = 1.06 \text{ \AA}$. The fact that $\psi = 0$ at $r = 1.06 \text{ \AA}$ means that the electron is never to be found at that particular radius. The $2p$ orbitals also have two nodes, one node in addition to the one at infinity. The pictures of the $2p$ orbitals, Figure 9.8 (p. 148) show that this nodal surface can be taken as one of the planes defined by pairs of axes. For the $2p_x$ orbital it is the yz -plane;

for the $2p_y$ orbital, it is the xz -plane. For $2p$ orbitals, no nodes are fixed solely by r , except the one at infinity.

In general, the ns orbitals have spherical symmetry and n different values of r , at which the wave function becomes zero (including the one at infinity). For np orbitals, one of these r -nodal surfaces is lost, and one of the coordinate-axis planar nodes substitutes for it. For nd orbitals two of the r -nodal surfaces are lost, and two more-complicated (or "angular") nodes substitute.

The connection between the number of nodal surfaces and n can be made meaningful in terms of a tangible model, the vibrating string. This connection can furnish a satisfying relief from the abstract quality of the Schrodinger equation, the wave function, and the probability distribution.

The Hydrogen Atom Orbitals

The hydrogen atom problem is more appropriately called the one-electron, or hydrogen-like, atom problem. It is applicable to any two-body problem involving a nucleus with charge Z and a single electron. Thus two important properties of the orbitals, the energy and the average electron-proton distance, depend upon Z as well

as upon the quantum numbers. Much of our understanding of chemical periodicity is based upon these dependencies.

The energy of a hydrogen-like atom depends upon Z and upon the principal quantum number n , but not upon the l or m quantum numbers:

$$E = -R \frac{Z^2}{n^2} \quad (11)$$

$$R = -313.6 \text{ kcal/mole}$$

The average electron-proton distance, or average radius, depends upon Z and upon two quantum numbers, n and l .

$$\bar{r}_{n,l} = 0.529 \frac{n^2}{Z} \left[\frac{3}{2} - \frac{l(l+1)}{2n^2} \right] \quad (12)$$

$\bar{r}_{n,l}$ being in Ångstrom units.

The Pauli Principle and Electron Spin

The Pauli Principle can be stated in various degrees of sophistication. The relatively simple statement given in the Textbook, "A single orbital can accommodate, at most, two electrons," offers a real advantage as an introductory formulation. It emphasizes the empirical basis for the principle and points to the most important piece of evidence requiring it—the Periodic Table. We do not use a statement in terms of quantum numbers (no two electrons can have the same values for all four quantum numbers). This definition has some subtle disadvantages. It is stated in abstract terms, and it suggests, incorrectly, that the Pauli Principle is derivable from quantum mechanics. The many-electron problem, as formulated in quantum mechanics, does *not* yield the Pauli Principle. It must be added as an empirical principle based upon the Periodic Table

and upon spectroscopic evidence. Moreover, the electron spin quantum number must be discussed—another new concept, which adds complexity without contributing toward an understanding of the Pauli Principle.

Another common statement of the Pauli Principle is: "At most, two electrons can occupy an orbital, and these electrons must have opposite spin." Again the concept of electron spin must be defined, hence attention is directed to the fact that two electrons with the same spin cannot occupy the same orbital, but with opposite spin they can. Yet the interaction between the two electrons seems to have little to do with the Pauli Principle. Calculations of this interaction show it to be quite negligible.

A quantum-mechanical statement of the Pauli Principle is: "The wave function of a many-electron atom must be antisymmetric with respect to exchange of the coordinates of any two electrons." This statement means that the wave function is changed by a factor of -1 if the coordinates of two electrons are interchanged. This mathematical property is not required by quantum mechanics. It is an empirical restriction imposed on the wave function to fit the experimental facts mentioned earlier.

The Pauli Principle is fundamental. Experimental observations showed it to be true many years ago, but no explanation has yet become apparent. In this sense, this important principle, even in its most abstract formulation, is completely empirical. Make this absence of explanation clear—it does not detract from the principle, but adds a challenge. Surely someday an explanation will be forthcoming, conceivably from the generation you are teaching.

Answers to Exercises and Problems

Exercise 9-1

List all possible changes on this staircase. List them systematically. For example, for the changes that begin on level 1, write $1 \rightarrow 2$, $1 \rightarrow 3$, $1 \rightarrow 4$,

and $1 \rightarrow 5$. For changes that end on level 1, write $5 \rightarrow 1$, $4 \rightarrow 1$, $3 \rightarrow 1$, and $2 \rightarrow 1$. Next to these indicate the size of each change. Repeat for levels 2, 3, and 4.

Answer

Jumps	Size	Jumps	Size	Jumps	Size	Jumps	Size
1 $\longleftrightarrow$ 2	1	2 $\longleftrightarrow$ 3	1	3 $\longleftrightarrow$ 4	1	4 $\longleftrightarrow$ 5	1
1 $\longleftrightarrow$ 3	2	2 $\longleftrightarrow$ 4	2	3 $\longleftrightarrow$ 5	2		
1 $\longleftrightarrow$ 4	3	2 $\longleftrightarrow$ 5	3				
1 $\longleftrightarrow$ 5	4						

Exercise 9-2

Suppose that electrons change from the higher energy states to the one designated No. 2. Use the energy values in Table 9-1 to make a list of the energy changes that occur. Compare your list with the Balmer spectral lines in Exercise 8-1, page 127.

Answer

Jumps	Energies, kcal/mole	Change, kcal/mole
3 $\longrightarrow$ 2	278.8 - 235.2	43.6
4 $\longrightarrow$ 2	294.0 - 235.2	58.8
5 $\longrightarrow$ 2	301.1 - 235.2	65.9
6 $\longrightarrow$ 2	304.9 - 235.2	69.7
7 $\longrightarrow$ 2	307.2 - 235.2	72.0
8 $\longrightarrow$ 2	308.7 - 235.2	73.5

Exercise 9-3

Write the electron configurations of aluminum and boron. In what way are they related to that of gallium?

Answer

Al	$1s^2$	$2s^2 2p^6$	$3s^2 3p$
B	$1s^2$		$2s^2 2p$
Ga	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^{10} 4s^2 4p$

The three elements and their electron configurations are related by having three electrons in the valence orbitals (last column above).

Problem 1

Use the energy level diagram in Figure 9-4 to calculate the energy required to raise the electron in a hydrogen atom from level $n = 1$ to each of the higher energy levels. Compare these energies with the spectral lines shown in the figure p. 126.

Answer

In general, the energy required to bring about

any change is

$$\text{energy required} = \left(\text{energy of} \right)_{\text{final state}} - \left(\text{energy of} \right)_{\text{initial state}}$$

Using this expression keeps the signs straight. This format might be used if the negative signs bother any of the students.

$$\text{level change} \left(\text{energy of} \right)_{\text{final state}} - \left(\text{energy of} \right)_{\text{initial state}} = \left(\text{energy} \right)_{\text{required}}$$

1 $\longrightarrow$ 2	(-78.4)	-	(-313.6)	=	235.2
1 $\longrightarrow$ 3	(-34.8)	-	(-313.6)	=	278.8
1 $\longrightarrow$ 4	(-19.6)	-	(-313.6)	=	294.0
1 $\longrightarrow$ 5	(-12.5)	-	(-313.6)	=	301.1
1 $\longrightarrow$ 6	(- 8.7)	-	(-313.6)	=	304.9
1 $\longrightarrow$ 7	(- 6.4)	-	(-313.6)	=	307.2
1 $\longrightarrow$ 8	(- 4.9)	-	(-313.6)	=	308.7

The changes correspond to the energies of the first seven lines in the ultraviolet region of the hydrogen atom spectrum. In your discussion, demonstrate that either the left- or the right-hand energy scale in Textbook Figure 9-4 can be used.

Problem 2

Repeat Problem 9-1, using level $n = 2$ for the starting level.

Answer

2 $\longrightarrow$ 3	(-34.8)	-	(-78.4)	=	43.6
2 $\longrightarrow$ 4	(-19.6)	-	(-78.4)	=	58.8
2 $\longrightarrow$ 5	(-12.5)	-	(-78.4)	=	65.9
2 $\longrightarrow$ 6	(- 8.7)	-	(-78.4)	=	69.7
2 $\longrightarrow$ 7	(- 6.4)	-	(-78.4)	=	72.0
2 $\longrightarrow$ 8	(- 4.9)	-	(-78.4)	=	73.5

Problem 3

Determine the value of E_n for $n = 1, 2, 3, 4$, for a hydrogen atom using the relation $E_n = -313.6/n^2$.

Answer

$$E_n = -\frac{313.6}{n^2}$$

Corresponding to each E_n , there are n^2 orbitals.

n	E_n	n^2
1	-313.6	1
2	-78.4	4
3	-34.8	9
4	-19.6	16

Problem 4

The first ionization energy for lithium is 124 kcal/mole. Determine the frequency for one possible line in the lithium emission spectrum. In what part of the spectrum would the line appear? $E = h\nu$, $h = 9.52 \times 10^{-14}$ kcal sec/mole. Refer to the figure on p. 125.

Answer

$$\begin{aligned}\nu &= \frac{E}{h} = \frac{124 \text{ kcal/mole}}{9.52 \times 10^{-14} \text{ kcal sec/mole}} \\ &= 1.30 \times 10^{15} \text{ cycles/sec}\end{aligned}$$

This line will appear in the ultraviolet part of the spectrum.

Problem 5

According to the quantum mechanical description of the 1s orbital of the hydrogen atom, what relation exists between the surface of a sphere centered about the nucleus and the location of an electron?

Answer

This question refers to any *s* orbital. Any particular surface represents positions having equal probability of being occupied by an electron. Be sure that the student realizes that the probability is different for spherical surfaces of different radii.

Problem 6

What must be done to a 2s electron to make it a 3s electron? What happens when a 3s electron becomes a 2s electron?

Answer

Energy must be added to a 2s electron if it is to be converted into a 3s electron. In becoming a 2s electron, a 3s electron must lose energy. It can do so by emitting light or by converting the energy into heat through a collision.

Problem 7

The quantum mechanical description of the 1s orbital is similar in some respects to a description of the holes in a much used dartboard. For example, the "density" of dart holes is constant anywhere on a circle centered about the bull's-eye, and the "density" of darts holes reaches zero only at a very long distance from the bull's-eye. What are the corresponding properties of a 1s orbital?

In the light of your answer, point out erroneous features of the following models of a hydrogen atom (both of which were used before quantum mechanics demonstrated their inadequacies).

- A ball of uniform density.
- A "solar system" atom with the electron circling the nucleus at a fixed distance.

Answer

The two properties of the "density" of dart holes both have counterparts in the 1s orbital of a hydrogen atom. The probability of finding an electron is constant on a spherical surface and corresponds to the constant "density" of dart holes on a circle. Moreover, the probability of finding an electron at a given radius decreases to zero only at an infinite radius, as is also true for the "density" of dart holes.

From these properties, the erroneous features of the two models can be deduced.

- The ball of uniform density has the following erroneous features:
 - The electron probability distribution is the same everywhere within the spherical volume of the ball.
 - The electron probability distribution reaches zero at a finite radius and is zero everywhere outside this radius.
 - The feature just mentioned implies the atom has a boundary.
- The "solar system" atom has the following erroneous features.

1. The electron probability distribution is concentrated at a single radius and is zero both at smaller radii and at larger radii.
2. The feature just mentioned implies that the atom has a boundary and that the electron never approaches the nucleus

Notice that the student may be picturing the atom as one of these two models. The first is encouraged by our space-filling models, and its most glaring defect is that it attributes to the atom a boundary surface. The second model is encouraged by representations of atoms commonly seen in advertising (and, perhaps, in pre-high school science courses). The "solar system" model places the electron in a spherical shell, again implying a boundary and a particular electron trajectory, both inconsistent with the quantum mechanical description and experimental facts (see *Background Discussion*). The best use of this problem may come in the class discussion of the erroneous features of models of the atom.

Problem 8

Make a table listing the principal quantum numbers (through three), the types of orbitals, and the number of orbitals of each type.

Answer

Principal Quantum Number	Type of Orbital	Number of Orbitals
1	s	1
2	s	1
	p	3
3	s	1
	p	3
	d	5

Problem 9

Name the elements that correspond to each of the following electron configurations:

$1s^2$
 $1s^2 \quad 2s^1$
 $1s^2 \quad 2s^2 2p^1$
 $1s^2 \quad 2s^2 2p^3$
 $1s^2 \quad 2s^2 2p^6 \quad 3s^2 3p^6 \quad 4s^1$

Answer

helium $1s^2$
 lithium $1s^2 \quad 2s^1$
 boron $1s^2 \quad 2s^2 2p^1$
 nitrogen $1s^2 \quad 2s^2 2p^3$
 potassium $1s^2 \quad 2s^2 2p^6 \quad 3s^2 3p^6 \quad 4s^1$

Problem 10

Consider these two electron populations for neutral atoms:

A. $1s^2 \quad 2s^2 2p^6 \quad 3s^1$;
 B. $1s^2 \quad 2s^2 2p^6 \quad 6s^1$.

Which of the following is FALSE?

- (a) Energy is required to change A to B.
- (b) A represents a sodium atom.
- (c) A and B represent different elements.
- (d) Less energy is required to move one electron from B than from A.

Answer

Choice (c) is false. B represents an excited sodium atom. The student should see that A and B show the same number of electrons; hence represent the same element.

Problem 11

Name the atoms whose orbital occupancy corresponds to those listed below. Assume all lower energy orbitals to be full and the atom to be in its lowest energy state.

(a) $2s^1$ (d) $3p^6$ (g) $1s^2$
 (b) $3p^4$ (e) $4p^1$ (h) $6s^1$
 (c) $3s^1$ (f) $2p^1$ (i) $5p^5$

Answer

(a) Li (d) Ar (g) He
 (b) S (e) Ga (h) Cs
 (c) Na (f) B (i) I

Problem 12

Write the orbital occupancy for the elements indicated. Refer to the orbital diagram, Figure 9-9.

- (a) element with atomic number 9
- (b) element with atomic number 13
- (c) element with atomic number 20
- (d) element with atomic number 7

Answer

(a) $1s^2 \quad 2s^2 2p^5$
 (b) $1s^2 \quad 2s^2 2p^6 \quad 3s^2 3p^1$
 (c) $1s^2 \quad 2s^2 2p^6 \quad 3s^2 3p^6 \quad 4s^2$
 (d) $1s^2 \quad 2s^2 2p^3$

Problem 13

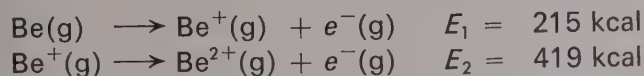
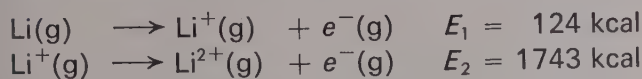
The electron configuration for lithium is $1s^2 2s^1$ and for beryllium it is $1s^2 2s^2$. Without referring back to Figures 9-16 and 9-17, estimate the approximate ionization energies to remove first one, then a second, electron. Explain your estimates.

Answer

The first ionization energy for lithium should be low, about 100 kcal, like that of sodium. The second electron is very difficult to remove because it must be removed from a $1s$ orbital. Hence the second ionization energy is expected to be about 1000 kcal.

The first ionization energy for beryllium should also be low, about 200 kcal, but larger than that of lithium because of the higher nuclear charge. The second ionization process still removes a $2s$ electron, hence is only a little more difficult than removing the first electron, requiring about 400 kcal. The second ionization requires more energy than the first because of the charge of the ion from which the electron is removed.

The experimental ionization energies are:

**Problem 14**

Which of the following electron configurations would you expect to have the lowest second ionization energy? Give reasons for your choice.

- (a) $1s^2 2s^2 2p^6$
- (b) $1s^2 2s^2 2p^6 3s^1$
- (c) $1s^2 2s^2 2p^6 3s^2$

Answer

Element (c) should have the lowest second ionization energy. Configuration (a) represents a noble gas which has a relatively high ionization energy. Configuration (b) is for an alkali metal. The first ionization will require a small amount of energy. The second will be more difficult as the electrons in $2p$ orbitals are held quite a bit more firmly than the valence electron.

Problem 15

The first four ionization energies of boron atoms are as follows:

$$\begin{array}{l} E_1 = 191 \text{ kcal/mole} \\ E_2 = 578 \\ E_3 = 872 \\ E_4 = 5962 \end{array}$$

Explain the magnitudes in terms of the electron configuration of boron and deduce the number of valence electrons of boron.

Answer

E_1 removes a $2p$ electron from a neutral atom.

E_2 removes a $2s$ electron from an atom with $1+$ charge. E_2 exceeds E_1 both because a $2s$ electron is removed instead of a $2p$ electron and because the atom now has a $1+$ charge.

E_3 removes another $2s$ electron. E_3 exceeds E_2 because the charge on the atom has increased ($1+$ to $2+$).

E_4 removes a $1s$ electron. E_4 exceeds E_3 because a $1s$ electron must be removed instead of a $2s$ electron and because the charge on the atom has increased ($2+$ to $3+$).

There are three valence electrons—those of moderately low ionization energy.

Problem 16

How many valence electrons has carbon? Silicon? Phosphorus? Hydrogen? Write the electron configuration for a neutral atom of each element.

Answer

Carbon: 4	$1s^2$	$2s^2 2p^2$	
Silicon: 4	$1s^2$	$2s^2 2p^6$	$3s^2 3p^2$
Phosphorus: 5	$1s^2$	$2s^2 2p^6$	$3s^2 3p^3$
Hydrogen: 1	$1s^1$		

Problem 17

How many valence electrons has radium? Barium? Bromine? Bismuth? (Count only s and p electrons.) Write the valence electron configuration for a neutral atom of each element.

Answer

Radium	$7s^2$
	2 valence electrons
Barium	$6s^2$
	2 valence electrons

Bromine	$4s^2 4p^5$
	7 valence electrons
Bismuth	$6s^2 6p^3$
	5 valence electrons

K	$4s^1$
Rb	$5s^1$
Cs	$6s^1$
Fr	$7s^1$

Problem 18

Write the orbital description for the *valence* electrons of each element in

- (a) column 1 of the Periodic Table
- (b) column 2
- (c) column 6
- (d) column 7

Answer

- (a) Column 1

H	$1s^1$
Li	$2s^1$
Na	$3s^1$

- (b) Column 2

Delete H, then as in (a) except each s^1 term becomes s^2 .

- (c) Column 6

O	$2s^2 2p^4$
S	$3s^2 3p^4$
Se	$4s^2 4p^4$
Te	$5s^2 5p^4$
Po	$6s^2 6p^4$

- (d) Column 7

Same as in (c) except p^4 becomes p^5 .

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

1. Whenever sodium compounds are volatilized in a burner flame, the characteristic yellow flame color is always present. Account for this in terms of electron energy.

Answer

One of the "allowed" energy changes for electrons in sodium atoms has a frequency in the yellow part of the visible light spectrum. Quantized "bundles" of energy are emitted as electrons release energy in changing from a condition of higher energy, E_2 , to a condition of lower energy, E_1 . The energy of light is given by

$$h\nu = E_2 - E_1$$

2. (a) Calculate the energy of the photon emitted if the frequency of the line is 5.2×10^{14} cycles/sec. This is in the yellow region of the visible spectrum. [Planck's constant, $h = 9.52 \times 10^{-14}$ kcal-sec/mole.]

- (b) Chemical bonds have energies of about 100 kcal/mole. Would they be dissociated by light of this energy?

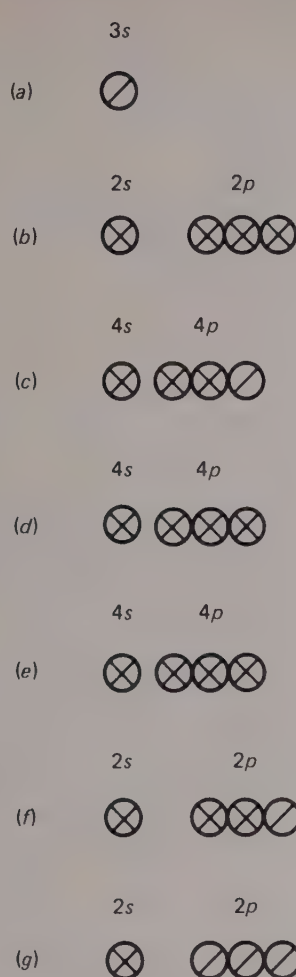
Answer

$$E = h\nu = \left(9.52 \times 10^{-14} \frac{\text{kcal-sec}}{\text{mole}} \right) \times \left(5.2 \times 10^{14} \frac{1}{\text{sec}} \right)$$

- (a) $E = 45.9$ kcal/mole.
 (b) No.

3. Diagram the electron configuration for the highest energy level containing any electrons for each of the following in their lowest energy state. (Use circles to represent orbitals; use diagonal lines to represent electrons. Label orbitals $1s$, $2s$, $2p$, etc.):

- (a) sodium atom, Na;
- (b) sodium ion, Na^+ ;
- (c) bromine atom, Br;
- (d) bromide ion, Br^- ;
- (e) krypton atom, Kr;
- (f) oxygen atom, O;
- (g) nitrogen atom, N.

Answer

4. Is more or less energy required to remove an electron from an atom of gaseous sodium than from an atom of gaseous neon?

Answer

Much less for sodium than for neon.

5. Suppose there are two electronic transitions, one involving 100 kcal/mole and the other 10 kcal/mole. What frequencies will be observed? In what spectral region will they be seen?

Answer

$$\frac{100}{9.52 \times 10^{-14}} = 10.5 \times 10^{14}$$

$$= 1.0 \times 10^{15} \frac{\text{cycles}}{\text{sec}}$$

ultraviolet region

$$\frac{10}{9.52 \times 10^{-14}} = 1.0 \times 10^{14} \frac{\text{cycles}}{\text{sec}}$$

infrared region

The electron configurations for the following neutral atoms are given for use in Questions 6–10.

<i>A</i>	$1s^2$	$2s^2 2p^6$	$3s^2$
<i>B</i>	$1s^2$	$2s^2 2p^6$	$3s^1$
<i>C</i>	$1s^2$	$2s^2 2p^6$	
<i>D</i>	$1s^2$	$2s^2 2p^5$	
<i>E</i>	$1s^2$	$2s^2 2p^3$	

6. Which of the electron configurations given above would you expect to have the lowest ionization energy?

Answer: B.

7. Which of the electron configurations given above would you expect for a noble gas?

Answer: C.

8. List the five configurations in predicted order of increasing ionization energy (lowest first).

Answer

The question is directed to the large-scale upward trend in ionization energy from left to right within a row. Thus the order is *B, A, E, D, C*.

9. Predict the configuration that should have the highest second ionization energy.

Answer: B.

10. Predict the configuration that should have the lowest second ionization energy.

Answer: A.

11. As atomic number increases in a given row of the periodic table, does ionization energy generally tend to increase or decrease?

Answer

There is a general tendency to increase. Small decreases are found when the first electron doubling within a sub-level occurs.

12. Two experimental methods of providing an atom with a measured amount of energy to cause ionization are photoionization and electron bombardment. Describe briefly how it is possible to measure ionization energy by each of these methods.

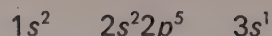
Answer

Photoionization: The frequency of light striking the gas sample is increased until it shows a sudden increase in conductivity. This increase is interpreted to mean electrons are available: ionization has occurred. The energy may be calculated by using light of known frequency or wavelength.

$$E = h\nu$$

Electron bombardment: Uses easily measured and controlled electrical voltages to accelerate electrons to sufficient energy to produce ionization. Ionization is detected by a large increase in the conductivity of the sample.

13. Consider a neutral atom with the electron configuration



Which of the following is FALSE?

- (a) The atom has atomic number 10.
- (b) The atom is not in the most stable configuration.
- (c) The atom must gain energy to change to $1s^2 \quad 2s^2 2p^6$.
- (d) The 1s and 2s orbitals are filled.

Answer

Statement (c) is false, the atom will lose energy as the $3s^1$ electron returns to give the more stable $1s^2 \quad 2s^2 2p^6$ configuration.

14. If there could be but one electron per orbital in an energy level diagram like Figure 9-10 in the Textbook, which of the following would be noble gases?

- (a) Element 1 only.
- (b) Elements 2, 10, 28, and 60 only.
- (c) Elements 2, 10, 18, 36, and 54 only.
- (d) Elements 1, 5, 9, 18, 27, and 43 only.

Answer: (d).

Chemical Bonding



Intent and Approach

This chapter presents the essence of chemical bonding and how it affects molecular properties. The material is quite important because a good understanding will serve as a strong basis for any further work, both in this course and later.

We have adopted an explanation of chemical bonding that may be new to you. It uses the phrase *electrons are attracted simultaneously to two nuclei* to explain *all* chemical bonds. This means that the same principles that explain the stability of covalent bonds also explain the stability of ionic bonds.

This material should be developed naturally from Chapter 9. The electron orbital filling and the tendency toward noble gas structure can occur in several ways to give molecules that

contain "satisfied" atoms, and hence stable structures. The valence orbitals determine the possible structures, since they fix the number of bonds an atom forms and determine the bond angles. A large amount of structural information is condensed in a few simple bonding rules, from which the student should gain substantial predictive ability.

From this chapter the student should learn:

1. why molecules are more stable than separated atoms;
2. to predict how many bonds can be formed by an atom in the first three rows of the Periodic Table; and
3. that multiple bonds can form.

Outline

The origin of the stability of a chemical bond is pinpointed. Among the attractive and repulsive electrostatic forces, the electron-nucleus terms *always* furnish the attractive forces. The possibility of simultaneous proximity of one or more electrons to two nuclei accounts for the fact that two atoms are more stable when near one another than when far apart. The possibility of simultaneous proximity is determined by the filling of valence orbitals (Introduction).

Clustering of ions, attracted by their opposite charges, lowers the potential energy of the system. Atoms from opposite sides of the Periodic Table

have electron configurations conducive to ion formation (10-1).

The energy of an atomic cluster can be lowered by sharing electrons in unfilled orbitals. Three ways to represent bonds are given (10-2).

As a result of the spatial arrangement of orbitals, bonds can form at angles to each other. Molecules are not all spherical. Isoelectronic series of compounds are introduced (10-2).

Combinations of isoelectronic groups lead to some new molecules whose structure and properties can be partially predicted (10-3).

Hydrocarbons serve to introduce structural

isomers (10-4), double bonds (10-5), and triple bonds (10-6).

Hydrogen bonding helps explain the atypical properties of H_2O , NH_3 , and HF (10-7).

A review section stresses that all the bonding arrangements have a common cause: *electrons are simultaneously attracted to two nuclei* (10-8).

New Concepts

1. Chemical bonding can be explained in terms of electron-nucleus attraction.
2. Bonding capacity is related to electron configuration.
3. Chemical bonds can be represented in several ways.
4. Isoelectronic molecules.
5. Multiple (2 or 3) bonds are possible between one pair of atoms.

SCHEDULE AND RELATED MATERIAL

Suggested Time : 10 days

Text Section	Topic and Related Work	Exercises	Problems		
			Easy	Medium	Hard
10-1	Ionic Bonding	1	1-5, 7, 8	6, 9	20
10-2	Covalent Bonding <i>Film: Chemical Bonding</i>	2-4	11-13	14-19, 21	
10-3	Families of Covalent Compounds	5	10	23, 24 25	
10-4	Hydrocarbons	6	22		
10-5	Double Bonds				
10-6	Triple Bonds				
10-7	Hydrogen Bonding				
10-8	Review				

Note: Experiment 25, Energy of Combustion, can be done at any time during Chapter 10.

Development

10-1 Ionic Bonding

When a compound is formed between two elements with extremely different ionization energy, there tends to be a large charge separation (ionic bonding), and the vacant valence orbitals of the metallic atoms tend to give a nondirectional character to the bonding. The result is that the crystals are made up of interlocking arrays of positive and negative ions whose packing is complicated because of two new factors: the two kinds of ions may have different size, and

they must be placed so as to avoid nearest neighbors of the same electric charge. Once again the packing of spheres readily explains the observed crystal structures, provided attention is given to size and charge.

Such an alternating arrangement of positive and negative ions produces crystals with quite distinctive properties. They do not have the electrical conductivity of the metals; the valence electrons remain highly localized near the negatively charged ions. In general, ionic bonds tend to be strong and, since they interlink the entire

crystal, ionic solids tend to be high melting, hard, and brittle.

Notice how this section ends by showing the student why beryllium chloride has a formula BeCl_2 and not some other ratio of elements. Further, this knowledge is based on an understanding of electron configuration and its connection to the Periodic Table.

The strong bonding in ionic solids is not the unique feature that gives ionic solids their high melting temperatures, however. After all, diamond has an extremely high melting temperature without ionic bonding. The high melting temperature of diamond is due to the interlinked nature of the three-dimensional network structure. Metals, too, tend to have high melting temperature, also without ionic bonding. In metals, the high melting temperature has to do with the continuous, three-dimensional linking of each atom to a number of neighbors. The same factor—three-dimensional linkage—accounts for the high melting temperature and extreme stability of ionic solids, just as it does in network solids and in most metals. The *Background Discussion* contains further information about the packing arrangements that occur most frequently in ionic solids (p. 186).

10-2 Covalent Bonding

To explain the existence of stable bonds, we must go back to the parts of the atom and their properties. This leads us to why chemists are interested in electrical forces. The attractive (and repulsive) forces that exist between the charged parts of the atom offer a basis for “explaining” a chemical bond. The Textbook describes bonding via attraction between orbital electrons and their nuclei. Remind the student that he studied the attractions and repulsions among electric charges in Chapter 6, Section 6-5.

Occasionally students will ask why we say that the potential energy goes down when two atoms bond. The easiest way to answer is to look at the opposite case. To separate two bonded atoms requires energy. If energy is conserved,

then that energy would be given out when they recombine.

A most important point is made on p. 174. This is that the simultaneous attraction of electrons to two protons (nuclei) accounts for the stability of the chemical bond. It is stated in terms of protons because the hydrogen molecule is the example used, but the statement is generally applicable. Generalize the expression to “. . . to two nuclei simultaneously” after the idea is fixed. This idea is visually reinforced in Textbook Figure 10-1 and in the figures on page 173, where the overlap region represents the electrons being attracted to both nuclei. This figure also explains some of the limitations to bonding. Each orbital has a maximum capacity—2 electrons. Bonds form through combinations which help supply this maximum for each orbital. Atoms like the noble gases, or others that have attained filled valence orbitals, do not share electrons effectively; there is no available space near the nucleus. Hence bonding is extremely weak—so weak that we say chemical bonding does not occur (van der Waals forces result).

The concept of overlap is a valuable one in chemistry, particularly in reference to covalent bonding. From our simplified point of view, it emphasizes that there must be a region in which electrons occupy valence orbitals of both atoms at once (this is the region in which they are simultaneously attracted to both nuclei).

There are numerous ways to represent atoms and their combinations in molecules. Be sure that the students realize these pictures are only pictures—drawn for convenience, and as convenience dictates. This means that different uses may dictate different representations. Don’t attach importance to pictorial aspects of the representations (for example, the fact that squares or circles could be used to represent orbitals). Emphasize that these simple pictures are useful because they provide a reliable and easily used basis for predicting formulas of stable compounds. It is appealing to the student that, by learning a few simple operating rules based upon these (or similar) representations, he can avoid

the necessity of memorizing thousands of molecular formulas.

Both the electron dot and the orbital representations of chemical bonding retain importance. The orbital representation gives more information but is somewhat more difficult to write. Both are used by practicing chemists as shorthand notations for discussing the chemical bonding in a molecule. The line representation of a chemical bond is another graphic aid. Although it is the one most used in designating structures, it presents the least information about the chemical bonding itself. All three will be used during the succeeding chapters. Be sure to relate the orbital representation to the energy level diagram.

Film, CHEMICAL BONDING,

fits here. See p. 177 for summary.

Table 10-6 deserves your attention. It is devised to give the electron configurations most frequently used *in compounds*. By not discussing the atomic configurations, the subject of hybridization is by-passed. We call these electron arrangements "derived" to allude to their experimental nature.

You will notice that some mention is made of bond angles and molecular shape. Chapter 17 will be devoted to molecular architecture.

10-3 Families of Covalent Compounds

The notion of isoelectronic structure is used in this short section to show similar bonding ability. Also, the beginner finds he can correctly combine the fragments into proper, heretofore unknown compounds.

10-4 Hydrocarbons

The combination of fragments is continued in a series of hypothetical reactions with carbon.

Carbon compounds are introduced for two reasons: first, to show that the bonding of this element is the same as all others and, second, to bring up structural isomerism and multiple bonds. Chapter 18 will cover carbon chemistry; so do not expand this and the next two sections.

Although nomenclature is not a prime purpose, note that a few names come up here. Also equations 1-4, p. 181, serve to illustrate the meanings of group names such as methyl, ethyl, and so on.

10-5 Molecules with Double Bonds

10-6 Molecules with Triple Bonds

The student should have little trouble grasping the basic idea of double bonds, since this type of bonding is just an extension of what the student has been drilling on. To form double bonds there must be (a) enough empty orbitals for two pairs of electrons to be shared and (b) appropriate geometry. Because the second factor is often not completely fulfilled, double bonds are quite reactive—that is, they form other bonds easily.

The rigidity of the double bond in ethylene can be clarified as follows. Use your forefingers to represent orbitals from two atoms. Touch the tips of these fingers to represent overlap, reminding the student that this is an energetically favored situation. Now twist one hand, keeping your fingertips in contact. Overlap is not affected, hence rotation can occur around a single bond (as, for example, in ethane). Now use your forefingers and middle fingers to represent two pairs of orbitals forming a double bond. Show that rotation about one of the bonds "breaks" the other bond. Since rotation can occur only with the absorption of enough energy to break the other bond, there is an energy barrier to the rotation. This barrier causes the double bond structure to be rigid. We discover empirically that this rigidity favors a planar structure in the compound ethylene.

10-7 Hydrogen Bonding

The formation of hydrogen bonds can be attributed to partial ionization. This is substantiated by the fact that the strongest hydrogen bonds occur when hydrogen is attached to an atom having high ionization energy, such as oxygen or fluorine. In addition, there seems to be a uniqueness about the effect that is probably associated with the relatively small size of the hydrogen atom. There is some evidence that lithium has similar behavior, but, by and large, the effects of hydrogen bonds distinguish these interactions from others.

Energetically, hydrogen bond interactions are intermediate between the normal chemical bond (usually over 50 kcal/mole) and the weak

van der Waals interactions (usually less than 1 kcal/mole). The magnitudes of hydrogen bond energies, 3–7 kcal/mole, account for their special importance. These interactions are sufficiently strong to dominate the usual solvent interactions, yet weak enough such that they do not challenge molecular stability. Most properties of hydrogen bonded systems can be understood in terms of these relative energies. The most dramatic and important examples occur in the biochemical systems, where it is found that hydrogen bonds play a crucial role in fixing molecular configuration.

10-8 Review

Supplementary Material

Books

1. L. Pauling, *THE NATURE OF THE CHEMICAL BOND*, Cornell University Press (1960). This third edition retains the basic content and clarity of the original 1938 version. The book remains valuable because of its strong influence on the advances made in the theory of chemical bonding within the last two decades. This book is written in such a way that much of it can be assimilated by an outstanding student.
2. M. J. Sienko and R. A. Plane, *CHEMISTRY*, 3rd ed., McGraw-Hill, New York (1966). Chapter 4, pp. 79–100, provides excellent supplementary reading for the above-average student.
3. C. A. Coulson, *VALENCE*, Oxford University Press, New York (1951). Contrasts the atomic and molecular orbital points of view. Excellent background reading for the teacher who can cope with the mathematics.
4. G. M. Barrow, *PHYSICAL CHEMISTRY*, McGraw-Hill, New York (1966), pp. 287–303. A fundamental discussion of dipole moment. Suitable for teachers.
5. G. E. Ryschkewitsch, *CHEMICAL BONDING AND THE GEOMETRY OF MOLECULES*. Reinhold Publishing Corp., New York (1963). A paperback, especially appropriate for this chapter.

6. J. W. Linnett, *THE ELECTRONIC STRUCTURE OF MOLECULES*, John Wiley & Sons, Inc., New York (1964). A new approach that is simple and explains many of the "hard" cases. Not for students.

Film

For ordering information see the *List of Film Sources* at the back of the Teacher's Guide.

CHEMICAL BONDING

A CHEM Study film

Running Time: 20 minutes

This is another film made in collaboration with Professor G. C. Pimentel, University of California, Berkeley. It makes use of and extends the concepts developed in the film "The Hydrogen Atom" (see p. 153), applying to the formation of a molecule of hydrogen and emphasizing the cause of bond formation as discussed in the Textbook. Extensive use of animation helps correct the impression of electron immobility which might be gained from the static sketches of molecules required in the Textbook.

Background Discussion

The Potential Energy Terms

The Schroedinger Equation was presented to show that the potential energy function merely

expresses the classical electrostatic interactions (see p. 158). Hence we can readily write down the contributions to the average potential energy.

If we consider a molecule AB , there will be three types of contributions.

Electron–electron Repulsions

Electrons have the same charge, hence work must be done to bring electrons close together. There are some electron–electron repulsions in atom A and others in atom B . As the atoms approach each other, these are still present, but there are also *new* electron–electron repulsions. When the electrons of atom A get close enough to feel the electrons of atom B , the average potential energy rises. Electron–electron repulsions cannot lower the potential energy as atoms come together.

Nucleus–nucleus Repulsions

Nuclei have the same charge; hence work must be done to bring them close together. Again we have a term that raises potential energy. Nucleus–nucleus repulsions cannot lower the potential energy as atoms come together.

Nucleus–electron Attractions

Electrons and nuclei have opposite charge, therefore they attract each other, and energy is released as electrons move closer to a nucleus. There are electron–nucleus attractions in atom A and others in atom B , but in the molecule there are *new* electron–nucleus interactions.* These new interactions lower the potential energy as the atoms come together. Since they are the only new terms that can lower potential energy, they must be responsible for the stability of a chemical bond. *The lowering of the potential energy on bond formation results from the fact that electrons are attracted to both nuclei at once rather than to only one of the nuclei at a time, as in the separated atoms.*

* This statement does not mean that the interactions possessed by separated atoms are unaltered in the molecule. When rather slight electron redistribution occurs on bond formation (as in the covalent bond), these terms do not change much. The case in which the redistribution is large is considered in the next section.

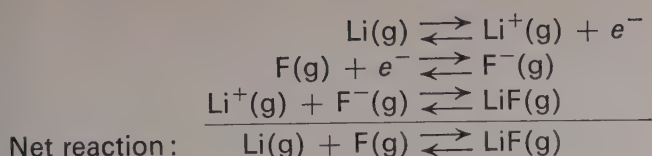
The argument can be reviewed in four steps:

1. The average energy change, $\Delta\bar{E}$, *must be negative* for a stable bond to form.
2. If $\Delta\bar{E}$ is negative, $\Delta(\overline{P.E.})$ *must be negative*. By the Virial Theorem, ΔE and $\Delta(\overline{P.E.})$ have the same sign, whereas $\Delta(\overline{K.E.})$ has the opposite sign. The Virial Theorem is derived directly (and rather simply) from Newton's second law and from the statement that all forces in the system depend upon particle separation as $1/r^2$.
3. *Electron–nucleus attractions must account for a negative value of $\Delta(\overline{P.E.})$.* The other contributions to the potential energy of the system make $\Delta(\overline{P.E.})$ go up as atoms come together.
4. Electron–nucleus attractions can result in a negative value of $\Delta(\overline{P.E.})$ because each electron is attracted simultaneously to two positive nuclei in the molecule, but only to one nucleus in the separated atoms.

Electrons Simultaneously Attracted to Two Nuclei: a General Explanation of Bonding

We need to investigate whether this argument is generally applicable. For example, the arguments 3 and 4 could, conceivably, not apply to ionic molecules. It is at least conceivable that the drastic redistribution of electrons in ionic bond formation could reduce the net magnitude of the electron repulsions even though there are more of them than there were prior to bond formation. It is also conceivable that the contribution of the simultaneous attraction of an electron to two nuclei is not an important factor at all. To investigate these possibilities, let us consider the formation of one of the most ionic diatomic molecules known, LiF , from a separated lithium atom and a fluorine atom. Fortunately we can consider this bond formation in a hypothetical series of steps for which we know, experimentally, all of the energy values.

BACKGROUND DISCUSSION



$$\Delta H = +124 \text{ kcal} \quad (1)$$

$$\Delta H = -83 \text{ kcal} \quad (2)$$

$$\Delta H = -178 \text{ kcal} \quad (3)$$

$$\Delta H = -137 \text{ kcal} \quad (4)$$

First, let us consider reaction (3), the formation of a bond between gaseous Li^+ and gaseous F^- . Since the electron distribution of LiF(g) is quite similar to that of a pair of spherical ions in proximity, *no large electron redistribution is involved in reaction (3)*. Hence the entire discussion of the previous section is applicable. The electron–electron repulsions present in the separated ions are also present in the molecule, *in addition to some new ones*. These new repulsions work against bond formation. The nucleus–nucleus repulsion also works against bond formation between Li^+ and F^- . The electron–nucleus terms must account for the energy lowering as Li^+ and F^- are brought together. Since electron distribution doesn't change much during reaction (3), the electron–nucleus attractions of the ions don't change much as the ions come together. Hence the energy must drop, because, in the molecule, the electrons of each ion are also close to the nucleus of the other ion. In particular, the largest contribution is due to the electrons of F^- , which are near the fluorine nucleus, simultaneously attracting the lithium nucleus. Thus the energy lowering in reaction (3) is clearly due to the simultaneous placement of electrons near two nuclei.

It only remains to investigate the energy effects required to obtain the electron distribution of Li^+ and F^- . This is the sum of the energies of reactions (1) and (2), +41 kcal. We see that energy is *absorbed* in achieving the electron distribution of Li^+ and F^- . Hence the bond formation between a neutral lithium atom and a neutral fluorine atom must be explained in terms of the energy drop in reaction (3), which we have seen is caused by simultaneously placing electrons near two nuclei.

To extend the generality of this argument, observe that the remarks in this and the previous section need not be restricted to a diatomic

molecule, nor even to a small molecule. The quantum-mechanical equation is of the same general form for solid sodium chloride and for solid sodium metal as for gaseous Cl_2 . Hence the explanation posed here is applicable to all bonds, strong or weak, in simple or complex systems.

This discussion must not be interpreted to mean that it is useless to recognize different bond types. Despite the fact that the same potential energy terms account for bonding in LiF as in F_2 , it is a decided advantage to recognize that in gaseous LiF the complicated mathematics describing the molecule can be well approximated in terms of the interaction of two singly charged ions. Even more important, with our present mathematical skills, we would be able to calculate very little about solid lithium fluoride *without* applying this approximation.

Even van der Waals effects are covered by this discussion. The difference between chemical bonding and van der Waals attractions is understandable if we consider how close two atoms with filled valence orbitals can approach each other. Two helium atoms attract each other only weakly, not because different interactions are present, but because the electrons near one nucleus can't get very close to a second nucleus. Again, this is not a denial of the advantage in seeking acceptable approximations stated in terms of tractable mathematics to treat this type of weak interaction (e.g., the London treatment). Yet it gives insight into the growing reluctance among chemists to make ironclad differentiations between chemical interactions and so-called physical interactions.

The Simplest Molecules, H_2^+ and H_2

The Schroedinger equation for a molecule is much easier to write than it is to solve. In general,

a many-particle problem can be treated only by successive approximations. Within the last few years accurate calculations as complex as pyridine (C_6H_7N) or NH_4Cl have been made. We can expect this calculational obstacle to be bypassed gradually as larger digital computers become more generally available.

Fortunately, the calculations for the two simplest molecules, H_2^+ and H_2 , are extremely informative about the nature of the covalent bond. (The hydrogen molecule ion, H_2^+ , consists of

two protons held together by one electron.) The confidence to be placed in the calculations is indicated by comparing calculated and experimental bond energies (the bond energy is the energy necessary to disrupt the bond). These are shown in Table 10-1. For H_2 , the calculated energies are shown for successively better approximations (as indicated by the number of terms retained in the expansion of the solution of the Schrodinger equation) together with an estimate of the effect of adding many more terms.

TABLE 10-1

Comparison of Calculated and Experimental Bond Energies of H_2^+ and of H_2

Reaction	Degree of Approximation	Calculation (kcal/mole)	Experiment* (kcal/mole)	% Error
$H_2^+ \rightarrow H + H^+$	best available	64.25	64.37	0.2
$H_2 \rightarrow H + H$	5 terms	103.7	108.65	5
	11 terms	107.85		0.8
	13 terms	108.15		0.5
	estimated for more terms	108.7 ± 0.3		<0.3

* These numbers differ from those in Table 10-3 because they include the zero-point vibrational energy.

TABLE 10-2

A Contrast of Energy Effects Due to Particle Interactions in H_2^+ and in H_2

	H_2^+			H_2		
	Separated Atoms (kcal)	Molecule (kcal)	Net Effect (kcal)	Separated Atoms (kcal)	Molecule (kcal)	Net Effect (kcal)
$\Delta \overline{P.E.}$ for:						
Electron-electron repulsions		none present		0	+681	+681
Nucleus-nucleus repulsions	0	+313	+313	0	+449	+449
Electron-nucleus attractions	-627	-1069	-442	-1254	-2601	-1347
$\Delta (P.E.)$	-627	-756	-129	-1254	-1471	-217
$\Delta (K.E.)$	+313.5	+378	+64.5	+627	+735.5	+108.5
$\Delta \overline{E}$	-313.5	-378	-64.5	-627	-735.5	-108.5
r_e		1.06 Å			0.74 Å	

The close agreement between experimental and calculated values shown in Table 10-1 gives us confidence that the calculational breakdown of this energy into the various contributions is meaningful and valid. These contributions are listed in Table 10-2 and are contrasted for H_2^+ and H_2 . The equilibrium bond lengths, r_e , are given as well. In considering the significance of the energy terms, we must remember that the bond length is much shorter in H_2 than in H_2^+ .

Considering H_2^+ first, we see that a stable chemical bond is formed, even though only one electron is present. The larger magnitude of the electron–nucleus attraction in H_2^+ (-1069 kcal) over that in the H atom (-627 kcal) accounts entirely for the chemical bond. Both kinetic energy and nucleus–nucleus repulsion work against chemical bond formation. In addition, we see that the net kinetic energy effect ($+64.5$ kcal) is much smaller than is the net nucleus–nucleus repulsion effect ($+313$ kcal). There are, of course, no electron–electron interactions, since there is but one electron.

Turning to H_2 , we see that with two bonding electrons, the bond is roughly twice as stable as the one-electron bond of H_2^+ (bond energies are -109 kcal for H_2 compared to -64.5 kcal for H_2^+). Since the bond is stronger, the bond length is shorter,* accounting for the 40% rise in the nucleus–nucleus repulsion. This shorter internuclear distance also accounts for the fact that the net change in the electron–nucleus attraction in H_2 (-1347 kcal) is more than twice that in H_2^+ (-442 kcal). There is a new interaction, the electron–electron repulsion ($+681$ kcal), but it is more than offset by the enlarged electron–nucleus attraction. Again, the rise in kinetic energy as the atoms come together is relatively small compared to the electron–electron repulsion and proton–proton repulsion.

Since the bond energy of H_2 , which has two bonding electrons, is roughly double that of H_2^+ , which has one bonding electron, there is every reason to expect that the same explanation should account for chemical bond formation in

these two molecules. This is an important observation because it discriminates against explanations of bonding based on some sort of interaction between the two electrons. For example, “electron exchange” and “overlap” are two commonly used terms that should not be misinterpreted. Overlap, for example, means that a bonding electron can occupy a region of space that is simultaneously an important part of two valence orbitals. The overlap of orbitals contributes to bonding because the bonding electron then simultaneously occupies the valence orbitals of two atoms. If there is but one bonding electron in the overlapping orbitals, a second bonding electron can still be accommodated, thus the molecule, though stable, will be reactive. If two bonding electrons occupy the overlapping orbitals, the bond is stable *in spite of* the electron interactions, not because of them. At all internuclear distances, the forces between electrons tend to push the atoms *apart*, and the energy of this interaction tends to make the molecule *less stable*.

One more conclusion is contained in calculations of the type shown in Table 10-2. The equilibrium bond length is the internuclear distance at which the energy is a minimum—that is, at which the attractive forces are exactly equal to the repulsive forces. The attractive forces are entirely due to electron–nucleus attractions. Three contributions tend to force the atoms apart: electron–electron repulsions, nucleus–nucleus repulsions, and electron kinetic energy.* Of these three, the nucleus–nucleus repulsion becomes infinite as the internuclear distance approaches zero, whereas the other two contributions remain finite. Hence, at distances shorter than the equilibrium distance, where the energy increases quite sharply, the nucleus–nucleus repulsion term dominates the other terms. At the equilibrium distance it is as important as the other two terms.

* The electron kinetic energy varies with the assumed internuclear distance. This treatment is valid in the “Born-Oppenheimer” approximation, in which the nuclei can be considered to be motionless with respect to the extremely rapid electron motion.

* This inverse relationship between bond energy and bond length holds reasonably well for any pair of atoms.

Thus the consideration of H_2^+ and H_2 through quantum mechanics shows us the nature of the covalent bonding in these two prototype molecules. Any valid discussion of chemical bonding must be consistent with this reference point. We have reached these conclusions:

1. Chemical bonds are stable because of electron–nucleus attractions.
2. Electron kinetic energy, electron–electron repulsions, and nucleus–nucleus repulsions all act to decrease the stability of the chemical bond.
3. Orbital overlap is a useful concept because it gives importance to the region of space in which an electron is simultaneously close to two nuclei.
4. Orbital overlap does *not* imply that the electron–electron interaction contributes to lowering the energy of the system as atoms come together.
5. At the equilibrium distance, the nuclei are subjected to zero net force, because attractive forces are equal to repulsive forces. One of the most important repulsive terms is the nucleus–nucleus repulsion.

In view of these conclusions, we see that it is unfortunate that a number of current textbooks de-emphasize or fail to mention the role of the nucleus in explaining why two atoms attract each other but do not fall together. It is even implicit in the popular (and useful) space-filling molecular models that only the electron clouds need be considered. The best present theories lead to the opposite conclusion: a stable chemical bond would not exist unless a nucleus interacted with electrons close to a second nucleus, and the nuclei would collapse together without nuclear–nuclear repulsions.

Orbital Availability and Bonding Capacity

Chemical bonding has been explained in terms of simultaneous proximity of the bonding electrons to two or more nuclei. We have yet to discuss the condition which will give a stable bond.

In a sense, the electrons in any pair of atoms experience orbital overlap as the atoms approach each other. For example, the $1s$ electrons of a helium atom overlap the empty $2s$ and $2p$ orbitals of a second, nearby helium atom. They cannot, however, overlap significantly the $1s$ orbital of the second helium atom; these orbitals are full. The atoms cannot approach closely, so the only overlap occurs between the valence orbitals of one atom and the extra-valence orbitals* of the other. This type of overlap gives the weak interactions that determine the heats of vaporization of the noble gases, all less than 4 kcal/mole.

If there are vacant valence orbitals on one or both of the atoms, the situation is found to be different. The atoms move together until the valence orbitals of the two atoms overlap significantly. Then the energy of interaction is much larger. It may be as high as 100 kcal/mole.

Because these two situations involve such different amounts of energy, a distinction between them is useful and convenient. When two nuclei share electrons in valence orbitals, the attraction is called chemical bonding; when two nuclei share electrons only in extra-valence orbitals, the attraction is called van der Waals attraction.

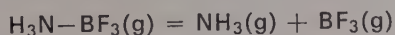
As defined above, then, chemical bonding can occur when two atoms approach each other with partly filled valence orbitals. We need only consult the electron occupancy of the valence orbitals to predict whether chemical bonds can form. There are three favorable situations we might find. First, two atoms may approach with one atom possessing a vacant valence orbital and the other having a half-occupied valence orbital (as in H_2^+). Then a one-electron bond forms, with a bond energy about half as large as that of a two-electron bond between similar atoms. Second, two atoms may approach with each atom containing a half-occupied valence orbital (as in H_2). This two-electron bond is the normal chemical bond, with a bond energy in the range 10 to 100+ kcal/mole. Third, two atoms may approach with one atom containing

* "Extra-valence" orbitals are those (unoccupied) orbitals outside the valence orbitals.

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a vacant valence orbital and the other containing a filled valence orbital (not already used in some other bond). Here again, a pair of electrons can be shared between the two atoms, but one atom provides (donates) both electrons. For example, the boron atom in BF_3 has a vacant valence orbital. The nitrogen atom in NH_3 , on the other hand, has an unused pair of electrons in a valence orbital. In such a situation we can predict that a stable bond can form between these two molecules. Generally such a bond energy is found to be less than 50 kcal/mole.* Such a bond is sometimes called a coordinate bond, a Lewis acid-base interaction, or a dative bond, though some chemists do not feel a distinctive name is needed.

* The energy absorbed in the following reaction is 42 kcal/mole.



In our attempt to place bounds upon the coverage of the Textbook, we have not made a definition of this type of bonding. The way has been prepared, however, in our emphasis upon the residual bonding capability represented by a vacant valence orbital. Specific examples are present in the text, but the bonding is not discussed. Many of the oxyacids are of this type. Thus the oxygen in HOCl is unlike the added oxygen in HOClO . The bonding of the second oxygen can be considered to arise from the sharing of one unused electron pair from the chlorine atom of HOCl in the vacant valence orbital of an oxygen atom. The complexes formed by the transition elements, discussed briefly in Chapter 20 can also be treated in such a fashion.

Table 10-3 shows some chemical bond energies. These illustrate the range of these energies and provide a basis for further discussion of ionic bond character.

TABLE 10-3
Some Chemical Bond Dissociation Energies (ΔH at 0°K)*

Reaction (all gases)	ΔH (0°K) (kcal/mole)	Reaction (all gases)	ΔH (0°K) (kcal/mole)
$\text{H}_2 = 2 \text{ H}$	103.2	$\text{HF} = \text{H} + \text{F}$	134
$\text{F}_2 = 2 \text{ F}$	36	$\text{HCl} = \text{H} + \text{Cl}$	102.2
$\text{Cl}_2 = 2 \text{ Cl}$	57.1	$\text{HBr} = \text{H} + \text{Br}$	86.5
$\text{Br}_2 = 2 \text{ Br}$	45.5	$\text{HI} = \text{H} + \text{I}$	70.5
$\text{I}_2 = 2 \text{ I}$	35.6	$\text{CH}_4 = \text{CH}_3 + \text{H}$	101
$\text{Li}_2 = 2 \text{ Li}$	25	$\text{CH}_3\text{F} = \text{CH}_3 + \text{F}$	108
$\text{Na}_2 = 2 \text{ Na}$	17.3	$\text{CH}_3\text{Cl} = \text{CH}_3 + \text{Cl}$	80
$\text{K}_2 = 2 \text{ K}$	11.8	$\text{CH}_3\text{Br} = \text{CH}_3 + \text{Br}$	67
$\text{Rb}_2 = 2 \text{ Rb}$	10.8	$\text{CH}_3\text{I} = \text{CH}_3 + \text{I}$	54
$\text{CH}_3-\text{CH}_3 = 2 \text{ CH}_3$	85	$\text{LiF} = \text{Li} + \text{F}$	137
$\text{HO}-\text{OH} = 2 \text{ OH}$	51	$\text{LiCl} = \text{Li} + \text{Cl}$	115
		$\text{LiBr} = \text{Li} + \text{Br}$	101
		$\text{LiI} = \text{Li} + \text{I}$	81
		$\text{ClF} = \text{F} + \text{Cl}$	60.5
		$\text{BrF} = \text{F} + \text{Br}$	55
		$\text{BrCl} = \text{Cl} + \text{Br}$	52.1
		$\text{ICl} = \text{Cl} + \text{I}$	49.6
		$\text{IBr} = \text{Br} + \text{I}$	41.9

* As compiled by T. L. Cottrell, *The Strengths of Chemical Bonds*, Butterworth Scientific Publications, London (1958). The energy is absorbed in the reactions as written. The quantity ΔH (0°K) is usually symbolized D_0 .

Ionic Bonding and Electronegativity

Electronegativity is not used in this chapter, but some teachers find it useful for explaining the continuous trend from ionic to covalent bonds.

When two moles of H atoms come together, the energy is lowered by 103.2 kcal, because in each molecule two bonding electrons are simultaneously near the two protons a good part of the time. When bromine atoms come together, the energy is lowered by 45.5 kcal/mole, because two bonding electrons are simultaneously near each pair of bromine nuclei a good part of the time. What, then, should we expect the energy decrease to be when a hydrogen atom and a bromine atom come together? In this situation two bonding electrons will be simultaneously near one proton (instead of two, as in H_2) and one bromine atom (instead of two, as in Br_2). It is reasonable to expect that a perfect sharing of the electron pair would give at least half the energy of bond formation in H_2 plus half the energy of bond formation in Br_2 .

$$\begin{aligned}\text{Expected covalent bond energy} &= \frac{103.2 + 45.5}{2} \\ &= 74.3 \text{ kcal/mole} \quad (5)\end{aligned}$$

In an unsymmetrical molecule like HBr, however, there may be some *additional* energy lowering associated with a redistribution of the electrons so as to favor one atom over the other. Although the electrons in a stable bond must be simultaneously close to two nuclei (even in such molecules as LiF), they do not have to be equally close to each. Should the electrons favor one atom over the other, the center of negative charge will be displaced from the center of positive charge, giving the molecule an electric dipole and the bond some ionic character. By this argument, then, the energy required to break the bonds in a mole of HBr should be 74.3 kcal or *greater*, the amount greater being a measure of how much the electron distribution is skewed away from equal sharing or covalent distribution.

This discussion is all based upon the empirical regularity, first recognized and interpreted by Linus Pauling, that the bond energy of a molecule AB always exceeds somewhat the algebraic mean of the bond energies of A_2 and B_2 . The amount of excess is interpreted as a measure of ionic character of the bond, and Pauling was successful in using this type of data in founding an electronegativity scale. Before considering

TABLE 10-4
"Equal-sharing" Bond Energies Compared to Experimental Values
(All Values in kcal/mole)

Molecule	Observed $D(AB)$	Algebraic Mean $\frac{1}{2}[D(A_2) + D(B_2)]$	Excess Energy $D(AB) - \frac{1}{2}[D(A_2) + D(B_2)]$
BrCl	52.1	51.3	0.8
IBr	41.9	40.5	1.4
ICl	49.6	46.3	3.3
IF	46	35.8	10
BrF	55	40.7	14
ClF	60.5	46.5	14
HI	70.5	69.4	1.1
HBr	86.5	74.3	12.2
HCl	102.2	80.1	42
HF	134	69.6	64
LiI	81	30.3	51
LiBr	101	35.2	66
LiCl	115	41	74
LiF	137	30.5	106

Pauling's electronegativities, let us examine the expected "equal-sharing" bond energies and the experimental values of some of the molecules given in the right-hand column of Table 10-3. These are given in Table 10-4, and they verify the generalization that experimental bond energies exceed the calculated values.

Pauling reasoned that the amount of excess energy should be fixed by the *difference* in electronegativities of the two atoms. Since the chemistry of atoms is fixed by energy relations, he attempted to use excess energy as a means of defining an electronegativity scale. He found that a self-consistent scale of electronegativity emerged if a square dependence was assumed:*

$$\begin{aligned}\text{Excess energy} &= (x_A - x_B)^2 \\ &= D(AB) - \frac{1}{2}[D(A_2) + D(B_2)] \\ x_A &= \text{electronegativity of atom } A \\ x_B &= \text{electronegativity of atom } B\end{aligned}\quad (6)$$

* Later, Pauling shifted to the geometric mean, $\sqrt{D(A_2)D(B_2)}$, instead of the arithmetic mean in (5) to eliminate a few negative values of excess energy. But this results in little change in the scale.

It must be recognized that equation (6) defines x_A . There are only two verifications of the scale. First, the set of x values so obtained is self-consistent, fitting a large amount of data. Second, the relative magnitudes of the x values so obtained correlate well with our intuitive ideas about relative electronegativities as shaped by the huge mass of known descriptive chemistry. The value of Pauling's scale is attested by its persistence today, three decades after its proposal. Figure 10-1 shows the most reliable portion of the relative scale, on which fluorine is 4.0.

Despite its usefulness, we have not presented the bond energy electronegativity scale in the Textbook, nor have we used the rather abstract term "electronegativity." We have instead laid a basis for relating the formation of ionic bonds to differences in ionization energy. This quantity more obviously relates to the charge distribution. The clear-cut connection suggests that ionization energy should provide a basis for defining an electronegativity scale. So it does.

The use of ionization energy as a basis for electronegativity was proposed by R. S. Mulliken, who devised a scale that is in reasonably close agree-

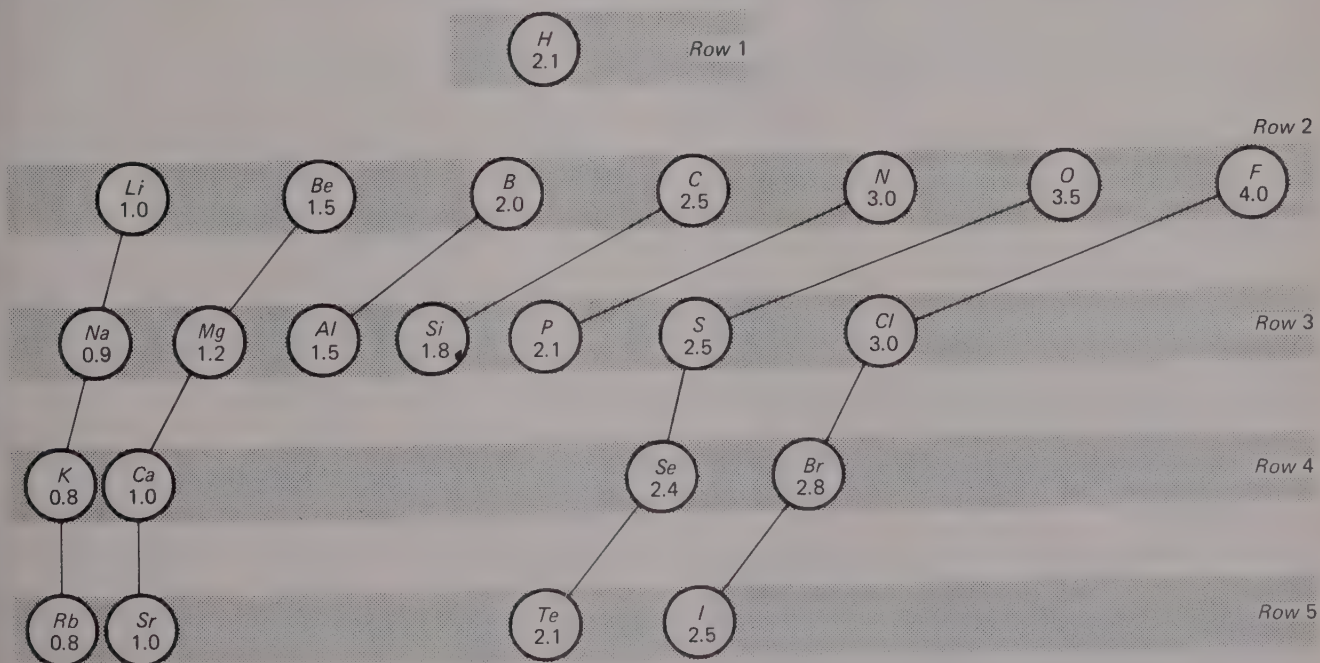


FIGURE 10-1

An electronegativity scale.

ment with the Pauling scale. Since Mulliken's ionization energy scale more obviously relates to charge movement, it has clearer intuitive significance. It has not found the wide use given Pauling's bond energy scale, however, because there are few known experimental values of ionization energies of negative ions (i.e., of electron affinities).

Two important practical results come from a consideration of electronegativity. First, the existence of a large electronegativity difference permits the prediction of extra bond stability over that expected for a covalent bond. This will be noticed in such properties as molecular stability, bond length, and vibrational frequency. Second, the electronegativity difference leads us to expect an electric dipole in the molecule. It suggests the magnitude of the bond dipole and indicates the direction of charge shift. Care must be used, however, in deciding whether the electronegativity scale is applicable to any particular case. The concept is defined in terms of normal single bonds in which each atom furnishes one electron to the electron-pair bond. Multiple bonds, electron donor-acceptor bonds, and molecules involving resonance need separate consideration in predicting charge distribution. As two examples, note that neither carbon monoxide, CO, nor nitric oxide, NO, have appreciable dipole moments.

Ionic Bonding

When atoms of very different electronegativity are bound together, asymmetric charge distributions result. We have already seen that the presence of such a charge separation implies that the bond formed is somewhat stronger than a covalent bond between the two atoms. Hence we can expect the bonding in ionic solids to be quite strong.

The possibility of such a three-dimensional linkage can be attributed to the existence of vacant valence orbitals on the metal atom. This can be seen by comparing the energy necessary to disrupt a gaseous lithium chloride molecule (115 kcal/mole) to that required to disrupt a

gaseous chlorine molecule (57 kcal/mole). The bond in gaseous lithium chloride is much more stable, yet LiCl condenses to a solid at room temperature, whereas Cl₂ remains a gas. The lithium atom in LiCl has residual bonding capacity through its empty valence orbitals that makes it energetically favorable for the LiCl molecules to aggregate into a crystalline arrangement.

The crystal arrangement obtained is dictated by the same kinds of considerations as for metals, but with the added complication that the charge distribution between lithium and chlorine must be taken into account. Just as in lithium metal, the lithium atom favors having as many nearest neighbors as possible (so as to make use of its valence orbitals), but these neighbors must be chlorine atoms. Clearly, the lattice is most stable if the positive lithium ions are surrounded by the negative chloride ions. Conversely, the chloride ions ought to be contacted solely by lithium ions.

The type of packing obtained with this restriction depends upon the relative size of the positive and negative ions. We can explore this restriction by considering the structures of ionic crystals with composition *AB*. If the two ions A^{n+} and B^{n-} are about the same size, the body-centered cubic packing tends to be favored. This structure gives each atom eight nearest neighbors of opposite charge. But if the positive ion is

TABLE 10-5
Expected Types of Packing for *AB* Ionic Crystals
Based on Radius Ratio

Radius Ratio ($\frac{\text{positive ion } A}{\text{negative ion } B}$)	Number of Nearest Neighbors (coordination number)	Symmetry around Ion
1.00 to 0.732	8	cubic (body-centered)
0.732 to 0.414	6	octahedral (NaCl structure)
0.414 to 0.225	4	tetrahedral
0.225 to 0.155	3	triangular

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systematically reduced in size, the negative ions will eventually come into contact with each other, and they will then tend to hold each other away from the positive ions. Just when this will occur depends generally upon the relative sizes of the ions—that is, upon the ratio of the two radii. When the radius ratio becomes too small, a new packing tends to be favored, with fewer nearest neighbors, the sodium chloride lattice. In this lattice, in which each atom has only six nearest neighbors, the negative ions are farther apart, and ions of opposite charge are again in contact. If the radius ratio is reduced even further, negative ion contacts again occur. Once again, there is a tendency for the substance to seek a packing in which each atom has still fewer

nearest neighbors. If we adopt the model that defines ions as spheres with fixed radii, it is easy to calculate the radius ratios at which these changes in packing are to be expected. They are given in Table 10-5.

Experimentally, we find that the crystal structures of the alkali halides reflect the expected influence of the radius ratio, but only in a rough correlation. Table 10-6 lists twenty alkali halides, five alkaline earth oxides, and eleven sulfides. The predicted coordination number is in agreement with the experimental one for 20 of the 36 cases.

The many failures in this correlation stimulate a closer look at the factors that fix the size of an atom, whether it be charged or not.

TABLE 10-6

Comparison of Predicted and Experimental Coordination Numbers for AB Ionic Crystals*

Compound	Radius Ratio	Coordination Number		Compound	Radius Ratio	Coordination Number	
		Predicted	Found			Predicted	Found
LiI	0.28	4	6	BeO	0.22	3 or 4	4
LiBr	0.31	4	6	MgO	0.46	6	6
LiCl	0.33	4	6	CaO	0.71	6	6
	(0.414)			SrO	0.81	8	6
LiF	0.44	6	6	BaO	0.96	8	6
NaI	0.44	6	6				
NaBr	0.49	6	6	BeS	0.17	4	4
NaCl	0.52	6	6	MgS	0.35	4	6
KI	0.62	6	6	CoS	0.39	4	6**
KBr	0.68	6	6	ZnS	0.40	4	4
RbI	0.69	6	6				
NaF	0.70	6	6	FeS	0.41	6	6**
	(0.732)			MnS	0.43	6	4
KCl	0.73	8	6	CdS	0.53	6	4
RbBr	0.76	8	6	CaS	0.54	6	6
CsI	0.78	8	8	HgS	0.60	6	4
RbCl	0.82	8	6	SrS	0.61	6	6
CsBr	0.87	8	8				
CsCl	0.93	8	8	BaS	0.73	8	6
KF	0.98	8	6				
RbF	1.09	8	6				
CsF	1.24	8	6				

* Ionic radii are taken from A. F. Wells, *Structural Inorganic Chemistry*, Clarendon Press, Oxford (1962), p. 71.

** This structure is peculiar in that three metal atoms are close enough together to be considered to be bonded to each other. It is the NiAs structure.

The existence of a finite separation between two nuclei at equilibrium implies that the energy is a minimum at that separation. The energy rises if the nuclei are moved away from this position, either closer together or farther apart. At the equilibrium distance, a balance exists between attractive forces and repulsive forces. All attractions contribute (electrons simultaneously near two nuclei), and all repulsions contribute (electron-electron and nucleus-nucleus repulsions) toward determining this balance. Small wonder that it does not occur at the same apparent size for a given ion in different environments. This is dramatically displayed in Table 10-7, which lists the experimental bond lengths in certain gaseous alkali halides and the nearest neighbor distances in the crystal. Most gaseous alkali halides are considered to be quite ionic in their bonding, yet the balance between attraction and repulsion uniformly occurs when the internuclear distance in gaseous molecules is about half an angstrom less than that found in the crystal. The longer bond in the solid is reasonably attributed to the repulsions among the halogen ions, and it is not surprising that the crystal bond length is a complicated, not a simple, function of the choice of ions. Some workers take cognizance of this by supposing that each ion has a different effective radius for each coordination number.

Aqueous Solutions of Ionic Substances

One of the most important properties of ionic substances is their formation of conducting solutions in water. The importance of the electric dipole of water in explaining the stability of the aquated ions should be stressed. It is *not* correct to say that the ease of formation of ions in the aqueous solution can be attributed to the fact that the ions were "already formed" in the solid. High melting temperatures of ionic crystals show that the crystals are quite stable, and this stability works against the solubility. Furthermore, some crystals thought to be quite ionic have extremely low solubilities (e.g., CaF_2 , BaF_2), whereas some substances that form molecular crystals (e.g., HCl , HBr , HI) are quite soluble in water, forming ions. Hydrofluoric acid, which should be more ionic than any of the substances HCl , HBr , or HI , is the least ionized acid in water. Finally, we must observe that the energy necessary to pull a gaseous lithium fluoride molecule apart to form $\text{Li}^+(\text{g}) + \text{F}^-(\text{g})$ is higher than the energy necessary to pull it apart to form neutral atoms, $\text{Li}(\text{g}) + \text{F}(\text{g})$. The formation of ions in an aqueous salt solution must be attributed to the very great stability of both positive and negative ions when surrounded by water molecules properly oriented, not to the parentage of the ion in an ionic crystal. Conversely, one can hardly cite the electrolyte properties of an aqueous

TABLE 10-7
Experimental M — X Distances for Alkali Halides in the Gaseous and Crystalline States

Alkali Halide	Bond Length, Gas (Å)	Nearest Neighbor Distance, Crystal (Å)	Difference (Å)	% Increase Over Gas Value
LiF	1.51	2.01	0.50	33
LiI	2.39	3.00	0.61	26
NaCl	2.36	2.81	0.45	19
NaBr	2.50	2.98	0.48	19
NaI	2.71	3.23	0.52	19
KCl	2.67	3.14	0.47	18
KBr	2.82	3.29	0.47	17
KI	3.05	3.53	0.48	16
CsF	2.35	3.00	0.65	28
CsI	3.32	3.95	0.63	19

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salt solution as compelling evidence that the salt forms an ionic crystal.

The orientation of water molecules around ions is called hydration of the ions, and this process is a dominant one in aqueous chemistry. The effect of this high degree of order is seen in the heat of hydration. For instance, the heat of hydration of Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} ions is -570 , -460 , -395 , -355 , and -305 kcal/mole, respectively. In general, ionic heats of hydration are large negative numbers, indicating that the combination of an ion with water dramatically abets the search for minimum energy. As a result, ions are hydrated in water solution.

Let us contrast the overall heat and entropy effects when gaseous, nonpolar substances as one class, and ionic solids as another, dissolve in water. For nonpolar gases, such as Ar, O_2 , C_2H_6 , Cl_2 , we have negative ΔH and negative ΔS of solution, see Table 10-8. The negative ΔH means heat is evolved, a result of new interactions forming in solution. The values of ΔS are so high that, for the substances mentioned, ΔG is positive, hence the solution of these substances is not favored. For ionic solids, however, ΔS is observed to be either positive or negative. The case of negative ΔS is like that above. For ΔG to be negative, ΔH must be negative—i.e., heat must be evolved during solution. When ΔS is positive, then ΔH can have either positive or negative sign, depending upon the relative magnitude of ΔG and $T\Delta S$. Thus a spontaneous dissolving ($-\Delta G$) can absorb energy ($+\Delta H$) if there is sufficient gain in randomness ($T\Delta S > \Delta H$). Thus the dissolving of $\text{NH}_4\text{Cl(s)}$ proceeds,

even though it absorbs energy, because there is a large enough entropy change to offset ΔH . For the student who recalls Expt. 24, where this cooling effect was observed, you can now say "the trend toward maximum randomness offsets the trend away from minimum energy."

Hydrogen Bonding

When a hydrogen atom is attached to an oxygen, nitrogen, or fluorine atom, the hydrogen atom retains the capability of additional bond formation. The second bond forms most readily between an H atom and an electronegative atom, such as an oxygen atom in another molecule. The second attachment is called a hydrogen bond, and its energy is only about one-tenth to one-twentieth as large as that of a normal chemical bond. Nevertheless, hydrogen bonds are quite important. Many properties are noticeably affected by hydrogen bond formation. In particular, the so-called physical properties of hydrogen bonded substances are obviously discordant when compared with those of substances that are similar except for a lack of hydrogen bonding capability. Some of the effects in hydrogen bonded substances are:

1. Boiling temperatures tend to be high.
2. Freezing temperatures tend to be high.
3. Solubilities are drastically affected. Hydrogen bonding substances tend to dissolve each other. Hence hydrogen bonding acids (that is, proton donors such as $\text{R}-\text{O}-\text{H}$) tend to dissolve hydrogen bonding bases (such as ketones) readily. Substances like alcohols tend to be poor solvents for nonhydrogen bonding substances (such as hydrocarbons) because the entrance of the hydrocarbon into the alcohol medium would require the separation of alcohol molecules, breaking hydrogen bonds.
4. Crystal structures are strongly influenced by hydrogen bonding capability (the reason melting temperatures tend to be high). It is almost an axiom that a molecular solid with capacity for hydrogen bond formation will have a structure that takes maximum ad-

TABLE 10-8

Some Entropy and Heat Effects on Dissolving

Substance	ΔH (kcal/mole)	ΔS (e.u.)*
Ar	-2.7	-22
O_2	-3.0	-23
C_2H_6	-4.4	-27
Cl_2	-6.0	-25

* Entropy unit = $\text{cal}\cdot\text{mole}^{-1}\text{ degree}^{-1}$

vantage of this possibility. Notice that the helical structures of macromolecules such as protein represent a special case of this general tendency.

5. The dielectric constants of hydrogen bonded liquids are distinctively high. Some examples are H_2O , H_2O_2 , HF , and HCN , which have dielectric constants of 78.5 (25°C), 73 (20°C), 83.6 (0°C), and 158 (0°C), respectively. Typical values for liquids without hydrogen bonds are those for dioxane, benzene, heptane, and diethyl ether, respectively 2.2, 2.3, 1.9, and 4.3.
6. Densities of hydrogen bonded substances tend to be high due to the attraction provided by the hydrogen bonding.
7. Viscosities tend to be high as a result of the intermolecular linkages.
8. Hydrogen bonding in the gas phase causes large deviations from perfect gas behavior.
9. The thermodynamic properties of a substance are affected. Heats of mixing, fusion, and vaporization are affected. Sometimes even more significant are the entropy effects, since the hydrogen bond interaction implies a high degree of order.
10. Spectroscopic changes are observed when hydrogen bonds form. Most characteristic are those that are found in the vibrational spectrum. The absorptions characteristic of the stretching vibration of an $A-H$ bond are very much altered when this group is joined by a hydrogen bond to some base, B .
11. Other properties that show measureable influence by hydrogen bonding are apparent

molar mass, acoustic conductivity, compressibility, surface tension, diamagnetic susceptibility, optical rotation, nuclear magnetic resonance, and thermal conductivity.

The traditional explanation for the existence of hydrogen bonding is based on "electrostatic" interaction. Because the hydrogen atom is attached to another atom A in an ionic bond, $A-H$, there is the possibility of an additional energetically favorable interaction with an electron donor. This can be compared to the interactions among polar molecules, as discussed in Section 17-13, with emphasis upon the unique feature of the hydrogen atom in possessing no electrons except its valence electron.

This explanation provides an acceptable starting point for discussion of hydrogen bond formation, but it does not span all aspects of the phenomenon. For example, one finds no correlation between the heat of formation of a hydrogen bond for a particular acid, $A-H$, and the electric dipole of a number of bases.

Hydrogen bonding can be discussed usefully in terms of the Lewis or electron transfer acid-base concept. The proton in $A-H$ is a particularly good electron acceptor, and consequently it interacts strongly with a good electron donor (i.e., a Lewis base). A reliable and self-consistent classification of base strength can be set up if hydrogen bonding is used as a criterion.

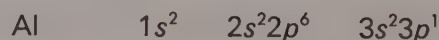
The most dramatic effects of hydrogen bonds are surely those found in biochemical systems. It is well established now that hydrogen bonding plays a crucial role in fixing the molecular configurations of such biological substances as proteins and nucleic acids. This important topic receives more attention in Chapters 17 and 18.

Answers to Exercises and Problems

Exercise 10-1

Write out the electron configuration for Al. If aluminum forms an ion, what would you expect its electric charge to be? What formula would you expect if aluminum and oxygen form an ionic compound?

Answer

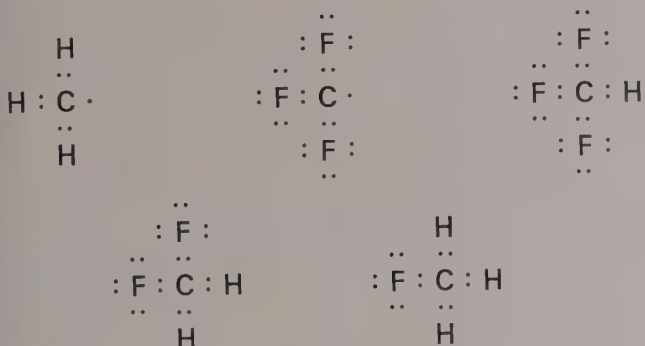


Al has three valence electrons; so it could form Al^{3+} if it lost all of them. It would then form Al_2O_3 .

Exercise 10-2

Draw electron dot formulas for the molecules CH_3 , CF_3 , CHF_3 , CH_2F_2 , and CH_3F . Which of these would you expect to be extremely reactive?

Answer

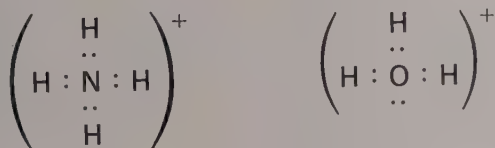


The first two would probably be very reactive because they each have an unpaired electron.

Exercise 10-3

Draw the electron dot formulas for the ions NH_4^+ and H_3O^+ . First draw the electron dot formulas for NH_3 and H_2O . Then add H^+ to each formula. H^+ has no electrons.

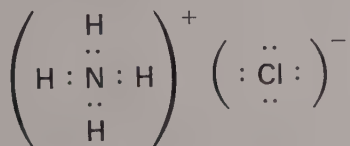
Answer



Exercise 10-4

Draw the electron dot formula for the ionic solid ammonium chloride, NH_4Cl .

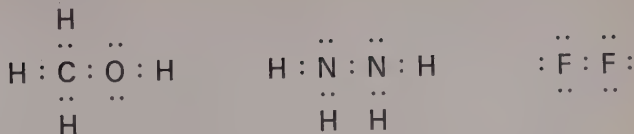
Answer



Exercise 10-5

Convince yourself that the electron dot formulas for CH_3OH (methyl alcohol) and $\text{NH}_2\text{—NH}_2$ (hydrazine) are the same as the electron dot formula for F_2 (fluorine).

Answer



If you look only at the dots representing electrons, they form in each example a figure eight pattern:

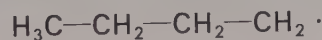


Exercise 10-6

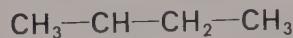
The next compound in the saturated hydrocarbon family would have five carbon atoms. The name *pentane* is used for this compound. Show how pentane can "grow" from each of the butane isomers. How many isomers of pentane would you expect? Draw them.

Answer

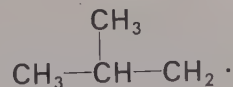
From *n*-butane we could get two fragments,



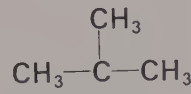
or



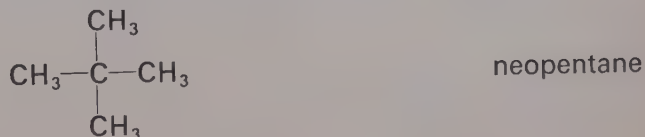
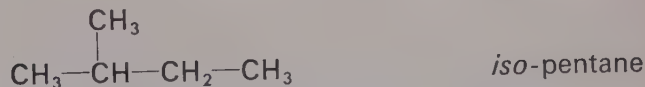
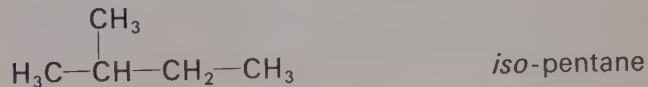
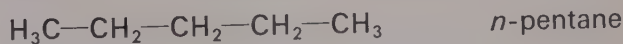
From *iso*-butane we could also get two fragments



or



When a $\text{CH}_3 \cdot$ fragment is added, we obtain:



The second and third are the same.

There are three isomers of C_5H_{12} .

Problem 1

Which of the properties listed are characteristic of an ionic solid?

- (a) low melting temperature.
- (b) conducts electricity as a solid.
- (c) dissolves in water to form a solution containing mostly ions.
- (d) dissolves to form a solution containing mostly molecules.
- (e) when fused, the melt conducts electricity.

Answer

- (c) and (e)

Problem 2

Which families of elements tend to form ionic solids?

Answer

Alkali metals, alkaline earth metals, halogens, and oxygen group elements.

Problem 3

Describe the electron configuration for atoms of lithium and fluorine after they have reacted to form an ionic solid.

Answer

Lithium with three electrons loses one to become Li^+ with the helium electron configuration. Fluorine with nine electrons gains one to become F^- with the neon electron configuration.

Problem 4

How many atoms of fluorine are needed per atom of calcium to form the ionic compound calcium fluoride?

Answer

Each fluorine atom gains one electron and each calcium atom gives up two electrons; therefore, two fluorine atoms are needed to one calcium.

Problem 5

Write the empirical formulas, assuming that these elements react to form ionic compounds. The atomic number is given to help you locate the element in the Periodic Table.

- (a) Al(13) and S(16)
- (b) Mg(12) and N(7)
- (c) Ba(56) and At(85)

- (d) Fr(87) and O(8)

- (e) Ra(88) and I(53)

Answer

- (a) Al_2S_3
- (b) Mg_3N_2
- (c) $BaAt_2$
- (d) Fr_2O
- (e) RaI_2

Problem 6

Add the energy term, E , to the equations

- (a) $K \longrightarrow K^+ + e^-$
- (b) $K^+ + I^- \longrightarrow KI$

Answer

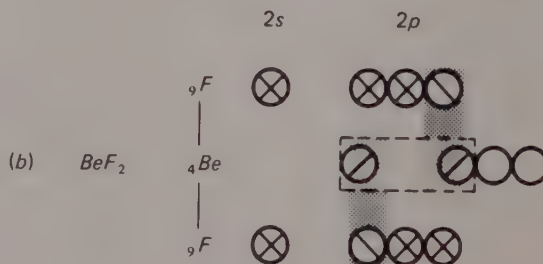
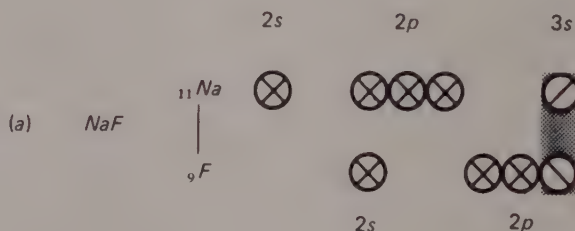
- (a) $K + E \longrightarrow K^+ + e^-$
- (b) $K^+ + I^- \longrightarrow KI + E$

Problem 7

Draw the orbital representations of

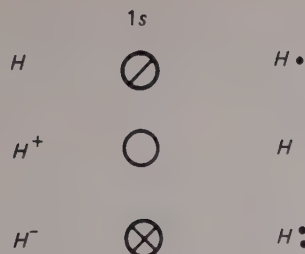
- (a) sodium fluoride, NaF.
- (b) beryllium fluoride, BeF_2 .

Answer



Problem 8

Give the orbital and also the electron dot representations for H, H^+ , and H^- .

Answer**Problem 9**

What type of bonding would you expect to find in MgO? Explain.

Answer

The clue as to the type of bonding comes from ionization energy. These can be found on p. 105 of the Textbook.

Mg	175.2 kcal/mole
O	314

Accordingly, one would expect bonding that is mainly ionic in MgO (the atoms have quite different ionization energies).

Problem 10

Show that NaF and MgO are isoelectronic compounds. How would you expect their melting temperatures to compare?

Answer

MgO should have a higher melting temperature than NaF. Mg²⁺ and O²⁻ have twice the charge of Na⁺ and F⁻ so they are attracted more strongly. The values are 992°C and 2800°C (MgO).

Problem 11

In general, what conditions cause two atoms to combine to form:

- a bond that is mainly covalent;
- a bond that is mainly ionic.

Answer

In each case, three conditions are needed: lower

energy, available valence electrons, and partially filled valence orbitals. In addition,

- the two atoms must have nearly the same ionization energy;
- the two atoms must have ionization energies that are quite different.

Problem 12

What are the molecular species present in gaseous neon, argon, krypton, and xenon? Explain.

Answer

Ne, Ar, Kr, and Xe are noble gases for which the gaseous species are single atoms. This is because their valence orbitals are completely filled. Having no partially filled valence orbitals, they have no bonding capacity.

Problem 13

What energy condition must exist if a chemical bond is to form between two approaching atoms?

Answer

The energy of the atoms must be lower when they are close together than when they are far apart.

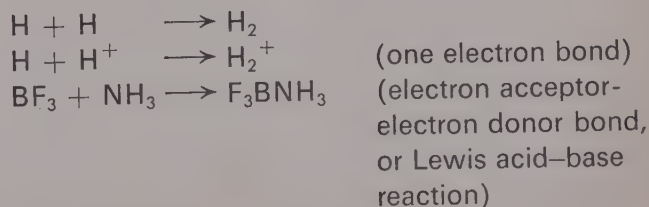
Problem 14

What valence orbital and valence electron conditions must exist if a chemical bond is to form between two approaching atoms?

Answer

- Valence electrons must be available* in at least one of the atoms.
- Partially filled or vacant valence orbitals must be present* in at least one of the atoms.

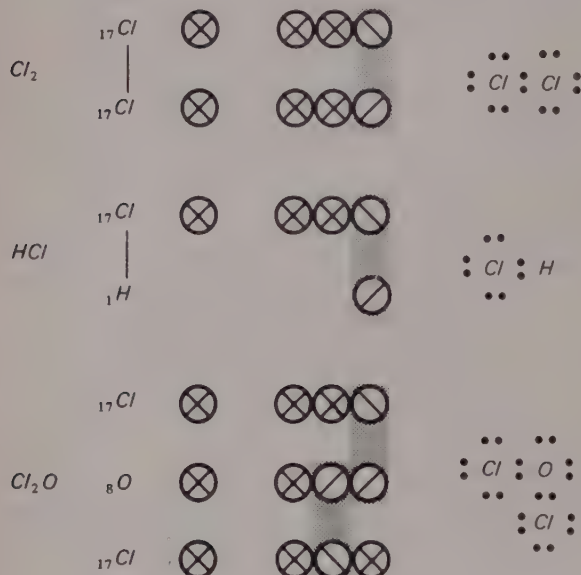
The italicized portions of the answer are sufficient, but the complete sentences encompass much more. For example, all of the chemical bonds below are included in the complete answer.



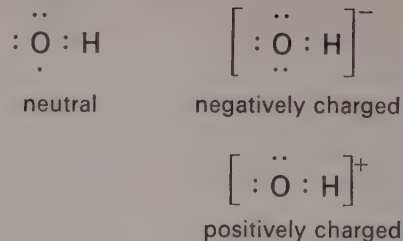
Problem 15

Give the orbital and also the electron dot representations for the bonding in these molecules: Cl_2 , HCl , Cl_2O .

Answer

**Problem 16**

Using the electron dot representation, show a neutral, a negatively charged, and a positively charged OH group.

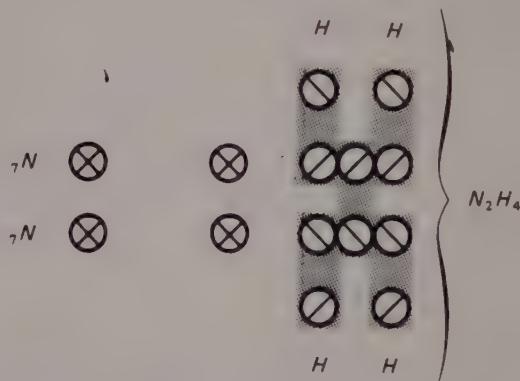
Answer to Problem 16

The probable reactivities of these species indicate why OH^- is the more important, chemically.

Problem 17

Draw the orbital representation of the molecule N_2H_4 , hydrazine.

Answer

**Problem 18**

Draw electron dot formulas of compounds that are iso-electronic with Cl_2 . Use the Periodic Table and the examples in Table 10-7 as guides.

Answer

	Cl	SH	PH_2	SiH_3
SiH_3	$\text{H}_3\text{Si}-\text{Cl}$ chlorosilane	$\text{H}_3\text{Si}-\text{SH}$ thiosilane	$\text{H}_3\text{Si}-\text{PH}_2$ silylphosphine	$\text{H}_3\text{Si}-\text{SiH}_3$ disilane
PH_2	$\text{H}_2\text{P}-\text{Cl}$ chlorophosphine	$\text{H}_2\text{P}-\text{SH}$	$\text{H}_2\text{P}-\text{PH}_2$ diphosphine	
SH	$\text{HS}-\text{Cl}$	$\text{HS}-\text{SH}$ hydrogen persulfide		
Cl	Cl_2 chlorine			

The known compounds are named. In each compound, the nonhydrogen atoms have the same figure eight pattern. See the answer to Exercise 10-5, p. 191.

Problem 19

Knowing the orbitals carbon uses for bonding, use the Periodic Table to predict the formula of the chloride of silicon. What orbitals does silicon use for bonding?

Answer

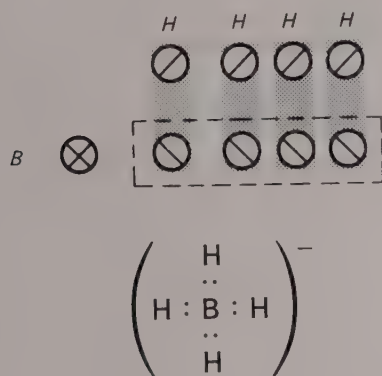


Silicon uses the 3s and three 3p orbitals to form four bonds.

Problem 20

The borohydride ion, BH_4^- , can be thought of as a combination of BH_3 and H^- ion. Give the orbital and also the electron dot representation for the borohydride ion.

Answer

**Problem 21**

Make use of your answer to Problem 20 to describe the bonding in the compounds sodium borohydride and lithium aluminum hydride.

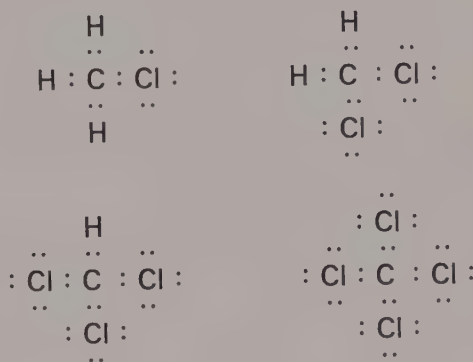
Answer

In these compounds, NaBH_4 and LiAlH_4 , ionic bonding exists between the alkali metal ion and the polyatomic hydride ions. The compounds dissolve or react with water as do many ionic compounds.

Problem 22

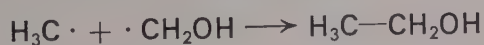
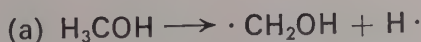
Draw electron dot formulas for the molecules CH_3Cl , CH_2Cl_2 , CHCl_3 , and CCl_4 .

Answer

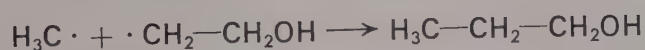
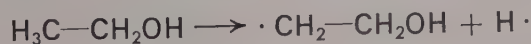
**Problem 23**

In Section 10-4, we showed how the hydrocarbon family $\text{C}_n\text{H}_{2n+2}$ can be derived from methane. Similar families of compounds can be derived from methyl alcohol.

Answer



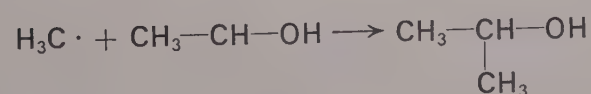
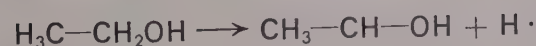
ethyl alcohol



n-propyl alcohol

(b) There are two isomers of propyl alcohol.

The second could be formed



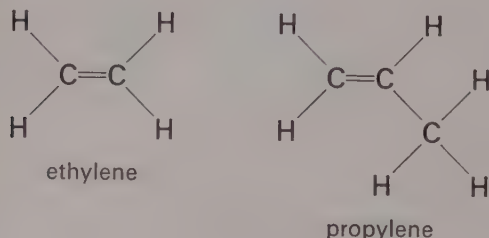
isopropyl alcohol

- (a) Show how ethyl and propyl alcohols, $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_3\text{H}_7\text{OH}$, can be derived from methyl alcohol, CH_3OH .
 (b) How many isomers would you expect for propyl alcohol?

Problem 24

Ethylene is the first of a family of hydrocarbons called *alkenes*. Each alkene has one double bond in the structure. Use line drawings to show bonding in the compounds ethylene and propylene, C_3H_6 .

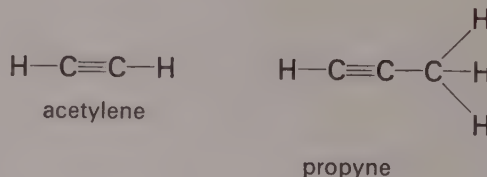
Answer



Problem 25

Acetylene is the first of a family of hydrocarbons called *alkynes*. Each alkyne has one triple bond in the structure. Use line drawings to show bonding in the compounds acetylene and propyne, C_3H_4 .

Answer

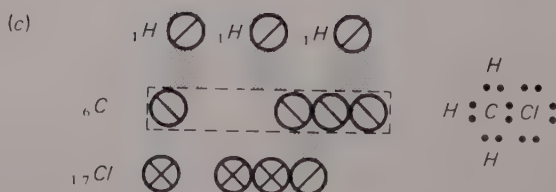
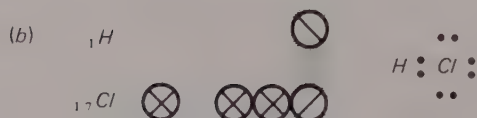
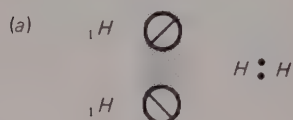


Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

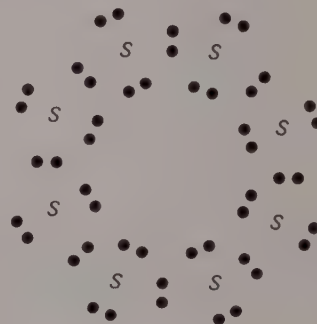
1. Draw orbital and electron dot representations for each of the following molecules:
 - (a) H_2 ,
 - (b) HCl ,
 - (c) CH_3Cl .

Answer



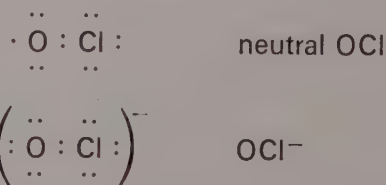
2. Draw the electron dot structure for a sulfur molecule, S_8 , in the ring form (see Chapter 17, p. 337).

Answer



3. Using the electron dot method show a neutral OCI and an OCI^- ion. Which is more reactive? Why?

Answer



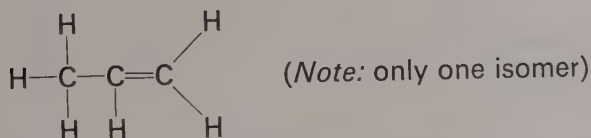
Neutral OCI is more reactive because it has a half-filled orbital. Students may

SUGGESTED QUIZ QUESTIONS

ask if the compound $\text{Cl}-\text{O}-\text{O}-\text{Cl}$ exists. Although its existence is formally possible, through the sharing of unpaired electrons on two OCl groups, the compound Cl_2O_2 is not stable.

4. Propylene, C_3H_6 , is a three-carbon chain with a double bond between two adjacent carbons. Draw the structural formula, using dashes to represent the covalent bonds.

Answer



5. Which of the combinations (1)–(5) are most likely to form (a) predominantly covalent bonds? (b) Predominantly ionic bonds?

- (1) potassium-chlorine
- (2) oxygen-oxygen
- (3) hydrogen-carbon
- (4) cesium-fluorine
- (5) chlorine-fluorine

Answer

- (a) 2, 3, 5.
- (b) 1, 4.

6. Use the electron configurations for the following neutral atoms to write the empirical formula for the stable substance containing the elements

<i>J</i>	$1s^2$	$2s^2 2p^6$	$3s^2$
<i>L</i>	$1s^2$	$2s^2 2p^6$	$3s^1$
<i>M</i>	$1s^2$	$2s^2 2p^6$	
<i>Q</i>	$1s^2$	$2s^2 2p^5$	
<i>R</i>	$1s^2$	$2s^2 2p^1$	

- (1) *L* and *Q*
- (2) *Q* and *R*
- (3) *J* and *Q*
- (4) *M* only
- (5) *Q* only

Answer

- (1) *LQ*
- (2) *RQ*₃
- (3) *JQ*₂
- (4) *M*
- (5) *Q*₂

To answer questions 7–10, consider the orbital representation of the valence electrons for the following elements.

	<i>s</i>	<i>p</i>
<i>A</i>		
<i>B</i>		
<i>C</i>		
<i>D</i>		
<i>E</i>		

7. Which, if any, could form a covalent bond with like atoms in the solid state?

Answer

C, *D*, and *E* (and *B* if it is boron).

8. What combinations of two elements could form an ionic solid?

Answer

AE, *A₂D*, *BE₃*, and possibly *A₂D₂*.

9. Write the empirical formula for a compound formed by the combination of *C* and *D*.

Answer: *CD*₂.

10. Write the empirical formula for a compound formed by combining *D* and *E*.

Answer: *DE*₂.

Energy Effects in Chemical Reactions



Intent and Approach

In presenting this material, introduce the idea that energy changes are an integral part of chemical reactions; then let the experiment provide the basis for student "discovery" of the additivity relation. Finally, explain that many repeated measurements, of the kind the student has performed, support the "law" of additivity.

He will remember his experiment and will use his specific experience as a basis for his understanding of the law. Avoid the reverse, authoritarian rule that "Because energy is conserved, the sum of reaction heats No. 1 and No. 2 must equal No. 3."

Outline

The water gas reaction is used to emphasize the difference in reaction heat for different reactions (11-1) and to establish an operational definition of heat content, H and ΔH (11-2).

The measurement of heat is disclosed in terms of calorimetry (11-3).

Section 11-4 shows the additivity of reaction

heats.

The conservation of energy by interchange from kinetic to potential is discussed (11-5).

The kinds of molecular motions are presented (11-6).

Section 11-7 is a brief review.

New Concepts

1. Chemical reactions involve energy.
2. Additivity Law of Reaction Heats.
3. Types of energy and the Law of Conservation of Energy.
4. Chemical energy is stored in molecules.
5. Heat content of chemical compounds, heat of reaction, ΔH .
6. Relative magnitudes of energies involved in phase changes, chemical changes, and nuclear changes.

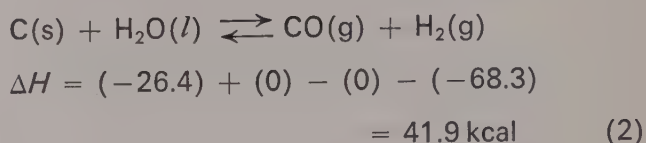
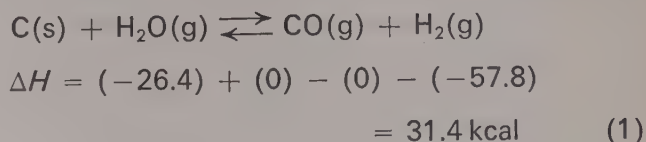
Development

11-1 Heat Energy and Chemical Reactions

The idea that chemical reactions can produce heat should not be new to the student. He may recall the burning of wood, his own body's combustion of food, the car engine heating up, and so on. Since the reproducible, quantitative aspect may not be in his thinking, it is unlikely that he will be able to give examples of reactions which absorb energy. To find examples for class use look up the terms heat of formation, heat of combustion, heat of reaction, etc. in a handbook, or see the section on thermochemistry in a physical chemistry text. Of course he already knows from his own experiments that some chemical reactions produce heat, Experiment 25, and that some phase changes absorb heat, Experiments 13 and 14—heat of melting. Experiment 24 showed some examples of both exo- and endo-thermic heat effects from reaction and solution.

This is a good place to review why we write (s), (l), (g), or (aq) after the symbols of some species. Ask for a class discussion on what

difference in heat effects would be expected for the reactions



The second reaction absorbs 10.5 kcal more than the first. This is equal to the heat of vaporization of liquid water.

A possibility exists for the confusion of symbols: *H* denotes heat content, and *H* represents one atom of hydrogen. We use *H* (heat content) only to establish the idea; in practice it is ΔH that is important. Thus there is little danger of trouble, and the different style of type makes confusion less likely.

SCHEDULE AND RELATED MATERIAL

Suggested Time: 10 days

Text Section	Topic and Related Work	Exercises	Problems		
			Easy	Medium	Hard
11-1	Heat in Reactions	1-5	1	2, 3	9
11-2	Heat Content		4		
11-3	Measurement of Heat of Reactions		5, 6	7, 8	
11-4	Expt. 26. Heat of Reaction Additivity of ΔH		10, 11, 20, 21	13, 14, 16, 19, 22, 23, 24	12, 15, 17, 18, 25
	*Expt. 27. Heat of Reaction, $\text{Mg} + \text{O}_2$				28, 29
11-5	Conservation of Energy			26, 27	
11-6	Energy Changes			30, 31	
	<i>Films:</i> Vibrations of Molecules <i>and</i> Molecular Motions				
11-7	Review			32	

* The placement of Experiment 27 is not critical except that it should come after Experiment 26.

11-2 Heat Content of a Substance

An operational definition of ΔH is developed. The definition of ΔH is straightforward, but the sign convention is *arbitrary*. That is, the difference *could* be

$$\left(\begin{array}{c} \text{heat content} \\ \text{of reactants} \end{array} \right) - \left(\begin{array}{c} \text{heat content} \\ \text{of products} \end{array} \right)$$

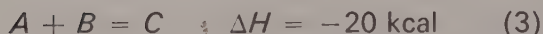
but ΔH as defined in the book is well established. This is its only claim to being "right."

There are two methods used for expressing ΔH . They are explained below, but first some comments on attitude. The method of expression is of only minor importance compared to the concept of heat content. For this reason, do not make a big issue of the conventions. Just use them naturally, possibly with occasional mention of the rationale given.

An *exothermic* reaction is written



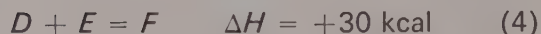
or



An *endothermic* reaction is written



or



In the first form the position of the energy term shows the type of reaction; in the second, the sign is used to indicate type. Both forms are found in published literature and are used by professional chemists.

11-3 The Measurement of Reaction Heat

Some details of more complex calorimeters are discussed. There is largely mechanical detail here. You might comment on the qualitative nature of the heat "measurement" (just by feel) in Experiments 14 and 24; the somewhat better

equipment used in Experiment 25; and the improved technique used in Experiments 26 and 27. These comments can be used to lead into a discussion of more elaborate calorimeters. But since these are designed for specific reactions, they will, of course, vary considerably. You may wish to ask the class to suggest the different features that might be required in a calorimeter designed to measure heats of reaction involving:

- (a) solutions only;
- (b) high pressure gases;
- (c) very reactive chemicals (HNO_3 , $\text{F}_2(l)$, HF , etc.);
- (d) small amounts of chemicals.

Expt. 26, THE HEAT OF REACTION,

fits here. See p. 132 of the Laboratory Guide.

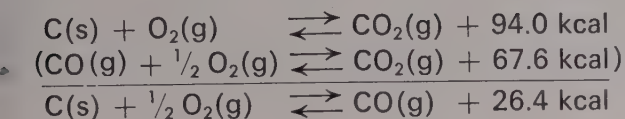
11-4 Additivity of Reaction Heats

Experiment 26 is designed to illustrate the additivity of reaction heats as well as to give the student some firsthand experience at calorimetry. The student is expected to do the experiment before the law is discussed.

The student's experience with Experiment 26 serves as a starting point. However, avoid a long discussion of sources of error and the various heat effects from solutions of different concentrations. The line of attack here is from the student's personal experience, through the vast amount of similar tests (made with much higher accuracy) to the unifying concept—the *law of additivity of reaction heats*. Use other examples.

The use of the law can be driven home by a discussion such as the following. The heat of many reactions is not easy to measure. There must be a definite reaction going on which does not change as it proceeds. The reaction must also proceed at a suitable rate (not too fast or too slow). However, application of the additivity feature of reaction heats allows us to calculate values for reactions that do not fill the require-

ments given. For example, carbon cannot be burned in oxygen to produce only carbon monoxide (some CO_2 is found also), hence the heat of reaction for $\text{C(s)} + \frac{1}{2}\text{O}_2(\text{g}) = \text{CO(g)}$ cannot be measured directly. By using the additive principle and two other equations, we can easily compute the desired ΔH .



Expt. 27, HEAT OF REACTION, $\text{Mg} + \text{O}_2$,
can fit here. See p. 135 in the Laboratory Guide.

11-5 Conservation of Energy

This section is to help the student understand that kinetic and potential energy are two types, each of which may appear in several forms. The Law of Conservation of Energy is developed as a regularity which expresses all the results now known.

Most students will already have heard the statement "energy is conserved," often given in a very authoritarian way. The intent here is to make the law clear and to emphasize its importance. Yet it is no different from other expressions of regularity. We wish to place it in the proper perspective; it is an important generalization, but was derived in the same way as all other such expressions. It has been modified before, and probably will be again.

11-6 Comparison of Energy Changes

The student has already met the idea of storing energy when a liquid boils. You may wish to

remind him of this. All steam-operated devices depend on the recovery of some stored energy when the gas cools.

This section gives a microscopic description of how energy is stored—in various motions of the atoms. It also takes up other ways to hold energy. The *Background Discussion* has some comments on how the descriptions were deduced.

The films can be shown to illuminate this section. Note the comments given (p. 202). The best practice is to view the films ahead of time and decide how to use them with your class.

Films, VIBRATION OF MOLECULES and MOLECULAR MOTIONS,

can fit here. See p. 202 for summaries.

The Textbook shows the student the magnitude of the energies involved in various types of changes by describing the conditions which prevail as a substance is heated—beginning with phase changes, continuing on to chemical changes involving the formation and/or breaking of bonds as we continue heating to higher temperatures, and finally the disruption of the nucleus itself at energies roughly 10^9 times those of ordinary chemical reactions.

Students can be directed at this point to consider the relative strengths of the kinds of forces involved in holding molecules, atoms, and nuclear particles together. This topic is discussed in some detail in later chapters.

11-7 Review

Supplementary Material

Article

Heat, in general: The entire September 1954 issue of *Scientific American* is devoted to heat, its measurement, and application. Pages 58–60 deal with the kinetic theory of heat. Pages 84–132 deal with thermochemistry.

Book

Mitchell Wilson, *ENERGY*, Time Inc., New York (1963). This well-illustrated book deals with all types of energy. It gives many examples related to the life around us. It deals with many topics outside this chapter. Good for class interest items.

Films

For ordering information see the *List of Film Sources* at the back of the Teacher's Guide.

Note: Both films cover molecular vibrations. Preview them to decide how you wish to use them.

VIBRATIONS OF MOLECULES

Running Time: 12 minutes

This film illustrates several vibration types in some simple molecules. It also contains material beyond our course. The first half might be shown for stimulation of interest.

Running Time: 13 minutes

MOLECULAR MOTIONS

A CHEM Study film

Experiments, models, and animation introduce and interpret translational, rotational, and vibrational molecular motions during both changes of phase and in molecular changes involving the absorption and emission of energy. Correlations between possible molecular motions and bulk chemical and physical properties show the applications of these concepts to directly observable quantities. Professor J. A. Campbell, of Harvey Mudd College, collaborated in the preparation.

Background Discussion

A big question for chemists is: What is the driving force of a chemical reaction; i.e., why do reactions go? The exact answer for this question is often rather difficult to give for a specific reaction and is somewhat involved for reactions in general. The answer must be related to changes in energy which accompany reactions, since all chemical reactions do show energy changes. Indeed, most reactions with which the student will be familiar liberate heat. In Chapter 11 you will be concerned with methods for measuring and calculating the energy balance in chemical reactions. This brings us to a somewhat more limited (but important) question: Why do chemists care about the heat of reaction? One reason is that the practical value of many reactions is related to energy liberation. Another is that energy change is one of the two factors (change in randomness is the other) which determine reactions. In later chapters we shall study how chemists relate the energy balance and changes of randomness to the question of why reactions go.

The following pages discuss these topics:

Additivity of Reaction Heats

Microscopic Description of Heat Content

Calorimetry

Some Conventions in Expressing Reaction Heats

Additivity of Reaction Heats

Since heats of reaction can be measured directly, the student might question the usefulness of a system for computing them. You should emphasize that some reactions either proceed too slowly to be studied in the calorimeter or do not react to give a single set of products. Here are two problems which illustrate these points.

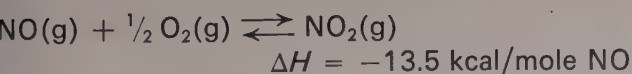
Acetylene reacts to form benzene in accordance with the equation



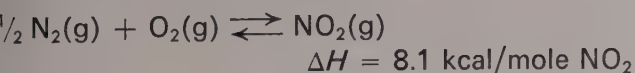
Even when catalyzed the reaction proceeds too slowly for its heat to be measured conveniently. The heat contents of benzene and acetylene are 13.1 and 54.3 kcal/mole, respectively. Thus the heat of reaction of acetylene to form benzene is

$$\begin{aligned} \Delta H &= 13.1 \text{ kcal} - 3 \times 54.3 \text{ kcal} \\ &= -149.8 \text{ kcal/mole C}_6\text{H}_6. \end{aligned}$$

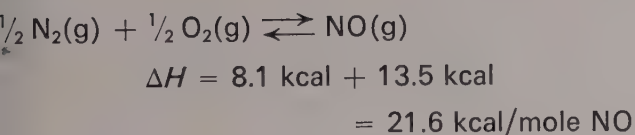
When nitrogen reacts with oxygen the main product is NO_2 but not NO . How can we find the heat of the reaction forming NO ? The gas NO reacts readily with O_2 in accordance with the equation



which can be combined with



to give



Other examples of problems of this type are given in most physical chemistry books.

Another advantage of the calculation method is that in practice it is not easy to measure ΔH , even when the reaction is appropriate. See *Calorimetry* below.

Microscopic Description of Heat Content

The student can be given an account of how heat is stored in various motions of the atoms, in positions of the molecules relative to each other, and in the nuclear structure of the atom. These ideas come from experiments we cannot place before the student yet. They will come up later—mostly in Chapter 16. Briefly they are as follows.

Infrared and microwave spectra can be explained on the basis of molecular vibration and rotation. Ultraviolet (UV) and visible spectra result from changes in electron arrangements. Such results are a cornerstone of our description of molecular structure.

Thermochemistry—the experimental aspect of the subject of Chapter 11—gives data about chemical bond energy. We are now beginning to obtain information on energy levels in the nucleus from the various accelerators.

Calorimetry

Measuring the heat of a chemical reaction with high accuracy can prove to be a rather difficult experimental feat. Remember that the objective is to measure all the heat evolved in the reaction.

The evolved heat does several things: it increases the temperature of (a) the products of the reaction (and even the reactants themselves, if the reaction is slow); (b) the water in the calorimeter; and (c) the calorimeter parts—stirrer, container, thermometer, etc. In addition, some heat is lost to or gained from the surroundings. In simple calorimetry, as performed in Experiment 26, some of these heat effects are lumped together, and others are neglected, which, in part, accounts for the error associated with the experiment.

In dilute-solution calorimetry one hopes that the effects of the specific heats of the reagents on the heat capacity of water will cancel each other. It is common practice to perform a reaction whose heat effect is known and to assume the difference between the heat obtained and the known heat of reaction to be the heat absorbed by the calorimeter and its parts. This absorbed heat is called the water equivalent of the calorimeter.

In precise calorimetry the chemist must consider the heat lost to or gained from the surroundings. This heat may be calculated from a plot of the experimental rate at which the calorimeter exchanges heat with the surroundings, both at the beginning and at the end of the reaction. Such data can be used to extrapolate to exact initial and final reaction temperatures. When the highest precision is required, the above method of correcting for heat loss is not used. The reaction is performed under *adiabatic* conditions; i.e., under conditions such that no heat is lost to or gained from the surroundings. Adiabatic conditions are commonly achieved by placing the calorimeter in an evacuated vessel within a metallic shield that can be heated electrically. Electrical energy is supplied to the shield at a rate that will maintain a temperature equal to that of the calorimeter, which thus does not gain or lose heat.

Mention is made that heats of reaction measured at constant pressure (ΔH_p) differ from such heats measured at constant volume (ΔH_v). This difference arises because a gas expanding against the pressure of the atmosphere does work and loses energy. In this case ΔH_p is more positive

than ΔH_v . For an exothermic reaction, ΔH_p is a smaller negative number. A gas sample which is compressed by the atmosphere has work done on it and gains energy. For this case, ΔH_p is less positive than ΔH_v . Heats given in the Textbook are for reactions measured at constant pressure. For reactions occurring in the solid and liquid phases, the effect of pressure is usually insignificant because the volume change, ΔV , is quite small. For reactions occurring in the gas phase the difference may be appreciable. Some students will wish more details on how to relate the expansion and contraction of the reaction system to the accompanying energy changes. One way to do this is to show the dimensions of $P\Delta V$.

The work done by the system can be defined by the equation

$$w = P\Delta V$$

Since pressure is defined as force per unit area, F/L^2 , and volume as length cubed, L^3 , the

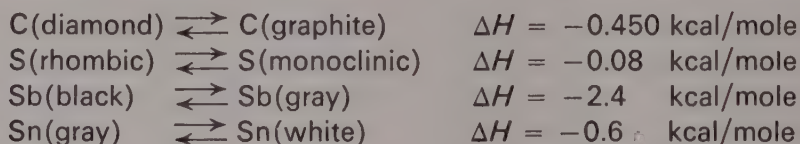
equation may be written

$$w = \frac{F}{L^2} \times L^3 = F \times L$$

This equation is a common definition of work and energy.

Some Conventions in Expressing Reaction Heats

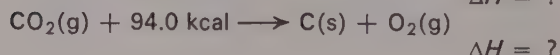
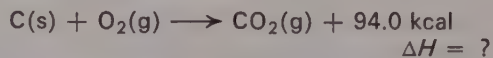
For heats of reaction to be meaningful they must be referred to a specific state of the substance. This means that, in addition to mentioning temperature and pressure, the polymorphic modification of the element must be given; for example, diamond or graphite, white phosphorus or red phosphorus. At this point you have an excellent opportunity to discuss the energy accompanying phase transitions in which there is a change in atomic arrangement but no change of state. Some of the more familiar transitions are expressed by these equations:



Answers to Exercises and Problems

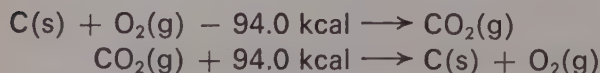
Exercise 11-1

Convince yourself that ΔH changes sign when a chemical equation is reversed.



Answer

If you consider yourself inside the reaction vessel, then you would "see" the reactions as



In the first reaction, heat is produced; in the

second, it is used. Heat comes out of the first system; $\Delta H = -94.0$ kcal. Heat must be put in the second system; $\Delta H = +94.0$ kcal.

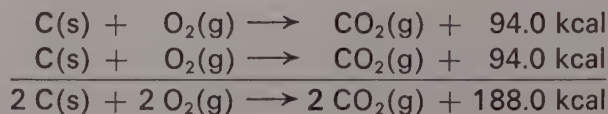
Exercise 11-2

Use the equation



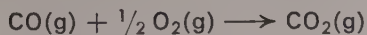
to convince yourself that ΔH will double when two moles of carbon are burned.

Answer



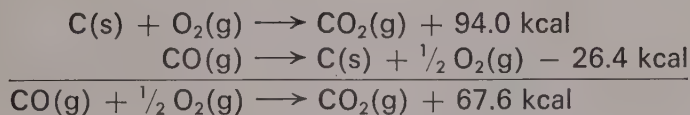
Exercise 11-3

Use values in Table 11-2 to calculate the heat of this reaction:



Compare your result with ΔH given for this reaction on page 196.

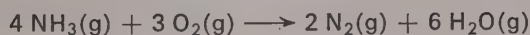
Answer



The value calculated is the same as that given on page 198.

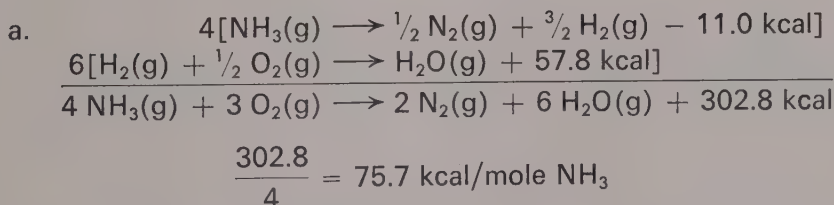
Exercise 11-4

- a. Calculate ΔH for one mole of NH_3 reacting with oxygen. Use



- b. Is this reaction exothermic or endothermic?

Answer



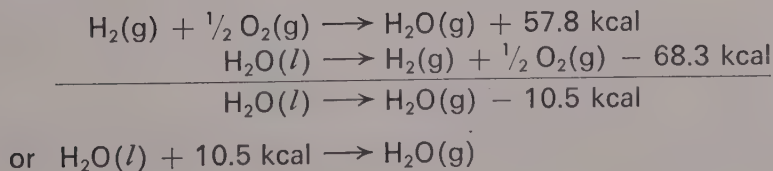
- b. The reaction is exothermic.

Exercise 11-5

Use values in Table 11-2 to calculate how much heat energy is required to vaporize one mole of H_2O at 25°C .



Answer



Problem 1

In the process of making water gas, the coke cools. Propose a method of heating this coke.

Answer

Blow air through the coke. Some of it will burn, forming CO_2 and heating the rest of the coke.

Problem 2

Consider both solid and gaseous fuels. Contrast advantages of using each.

Answer

Solid Fuel

easy to store
difficult to ignite
hard to produce small amount of heat
difficult to extinguish
no leak problems
difficult to move

Gaseous Fuel

requires special container
easy to ignite
easy to control size of flame

easy to extinguish
leaks from smallest hole
easy to move from storage to burning site

Problem 3

Which contains more stored energy (potential energy)?

- A burned or an unburned match head
- The chemicals a plant needs to make a potato, or the potato
- A used or unused photographer's flashbulb
- Freshly cut grass or grass that has been through a compost pile

Answer

- unburned match head
- potato
- unused flashbulb
- freshly cut grass

Problem 4

The amount of solar radiation received in Arizona is about $180,000 \text{ kcal/ft}^2/\text{year}$. How much coke (C) must be burned to CO_2 to produce this amount of heat energy?

Answer

$$\left(\frac{180,000 \text{ kcal}}{94.0 \text{ kcal/mole C}} \right) \left(\frac{12.0 \text{ g C}}{\text{mole}} \right) = 2.3 \times 10^4 \text{ g C}$$

This is about 40 pounds of carbon.

Problem 5

Which of the following reactions are endothermic?

- $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{g}) \quad \Delta H = -57.8 \text{ kcal}$
- $\frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{NO}(\text{g}) \quad \Delta H = +21.6 \text{ kcal}$
- $\text{NH}_3(\text{g}) \longrightarrow \frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) \quad \Delta H = +11.0 \text{ kcal}$
- $\frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) \longrightarrow \text{NH}_3(\text{g}) + 11.0 \text{ kcal}$
- $\frac{1}{2} \text{N}_2(\text{g}) + \text{O}_2(\text{g}) + 8.1 \text{ kcal} \longrightarrow \text{NO}_2(\text{g})$

Answer: (b), (c), (e).

Problem 6

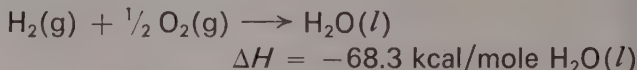
What is the minimum energy required to synthesize one mole of nitric oxide, NO, from the elements?

Answer

One must add 21.6 kcal to $\frac{1}{2}$ mole of $\text{N}_2(\text{g})$ and $\frac{1}{2}$ mole of $\text{O}_2(\text{g})$ in order to make one mole of NO.

Problem 7

How much energy is liberated when 0.100 mole of H_2 at 25°C and 1 atmosphere is combined with enough $\text{O}_2(\text{g})$ to make liquid water at the same conditions?

Answer

Since one mole of H_2O is formed from one mole of H_2 , 0.100 mole of H_2 will form 0.100 mole of $\text{H}_2\text{O}(\text{l})$ and liberate $(0.100) \times (68.3) = 6.83 \text{ kcal}$.

Problem 8

How much energy is consumed in the decomposition of 5.0 grams of $\text{H}_2\text{O}(\text{l})$ at 25°C and 1 atmosphere into its gaseous elements at the same conditions?

Answer



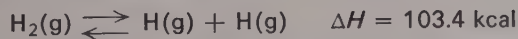
One mole of $\text{H}_2\text{O}(l)$ absorbs 68.3 kcal during decomposition to elements.

The amount of energy used to decompose 5.0 grams is

$$\frac{5.0 \text{ g}}{18 \text{ g/mole}} \times 68.3 \frac{\text{kcal}}{\text{mole}} = 19 \text{ kcal}$$

Problem 9

Which one of the following statements is FALSE as applied to this equation?



- (a) The positive ΔH means the reaction is endothermic.
- (b) Two grams of $\text{H}(g)$ contain more energy than 2 grams of $\text{H}_2(g)$.
- (c) Mass for mass, $\text{H}(g)$ would be a better fuel than $\text{H}_2(g)$.
- (d) The spectrum of $\text{H}_2(g)$ is the same as the spectrum of $\text{H}(g)$.

Answer

(d)

Problem 10

To change the temperature of a particular calorimeter and the water it contains by one degree requires 1550 calories. The complete combustion of 1.40 grams of ethylene gas, $\text{C}_2\text{H}_4(g)$, in the calorimeter causes a temperature rise of 10.7 degrees. Find the heat of combustion per mole of ethylene.

Answer

The heat released by 1.40 g of ethylene is

$$10.7 \text{ C}^\circ \times \frac{1550 \text{ cal}}{\text{C}^\circ} = 10.7(1550) \text{ cal}$$

This heat was released by 1.40/28.0 mole of ethylene. Thus the heat released per mole is

$$\frac{10.7(1550) \text{ cal}}{1.40/28.0 \text{ mole}} = 332,000 \text{ cal/mole}$$

$$= 332 \text{ kcal/mole}$$

The burning liberates heat, and since less heat content is left in the products than was in the reactants, ΔH is negative.

$$\Delta H = -332 \text{ kcal/mole C}_2\text{H}_4(g)$$

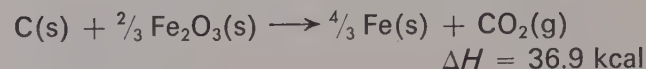
Problem 11

Given



Rewrite the equation, using one mole of carbon and the ΔH notation.

Answer



Problem 12

Given



Rewrite the equation for one mole of hydrogen gas and include the heat effect as a term in the equation.

Answer



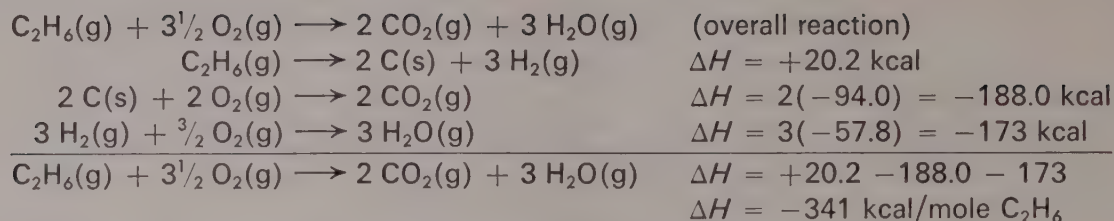
This problem reviews two important points: the methods of showing heat effect; and the quantitative connection between the mass terms (equation) and the energy term (ΔH). Note that the energy term is doubled when the mass terms are doubled. Energy is an extensive property; when more material changes, more energy is used or given up. Density, on the other hand, is an intensive property—a property which is independent of amount of material.

Problem 13

Using Table 11-2, calculate the heat of burning ethane in oxygen to give CO_2 and water vapor.

Answer. $\Delta H = -341 \text{ kcal/mole C}_2\text{H}_6$.

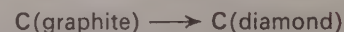
Answer



This value is called the heat of combustion of ethane.

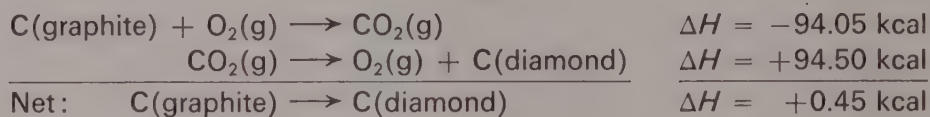
Problem 14

Given

Find ΔH for the manufacture of diamond from graphite.

Is heat absorbed or evolved as graphite is converted to diamond?

Answer

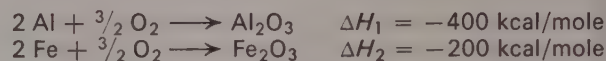


Since ΔH is positive, heat is absorbed. Notice how small it is, however, compared to combustion reaction heats. The low value of ΔH

shows that it was not a high energy requirement that delayed the production of artificial diamonds.

Problem 15

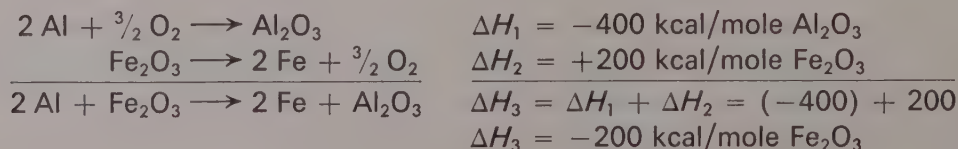
The "thermite reaction" is spectacular and highly exothermic. It involves the reaction between Fe_2O_3 , ferric oxide, and metallic aluminum. The reaction produces white-hot, molten iron in a few seconds. Given:



Determine the amount of heat liberated in the reaction of 1 mole of Fe_2O_3 with Al.

Answer. $\Delta H = -200 \text{ kcal/mole Fe}_2\text{O}_3$.

Answer

**Problem 16**

How much energy is released in the manufacture of

1.00 kg of iron by the "thermite reaction" mentioned in Problem 15?

Answer

$$\begin{aligned}\Delta H &= -200 \text{ kcal/mole Fe}_2\text{O}_3 \\ &= -200 \text{ kcal/2 moles Fe} \\ &= -100 \text{ kcal/mole Fe}\end{aligned}$$

$$1.00 \text{ kg Fe} = 1.00 \times 10^3 \text{ g Fe} = \frac{1.00 \times 10^3 \text{ g}}{55.8 \text{ g/mole}} = 17.9 \text{ moles}$$

$$\Delta H = \left(-100 \frac{\text{kcal}}{\text{mole Fe}} \right) \left(17.9 \frac{\text{moles Fe}}{\text{kg Fe}} \right)$$

$$\Delta H = -1790 \text{ kcal/kg Fe}$$

Problem 17

How many grams of water could be heated from 0°C to

100°C by the heat liberated per mole of aluminum oxide formed in Problem 15?

Answer

One hundred calories are necessary to raise 1.00 g of water from 0°C to 100°C. The heat liberated per mole of Al_2O_3 formed is 200 kcal = 200×10^3 cal. The amount of water that could be heated from

0°C to 100°C is

$$\frac{200 \times 10^3 \text{ cal}}{100 \text{ cal/gram}} = 2.00 \times 10^3 \text{ g} = 2.00 \text{ kg}$$

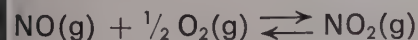
Problem 18

Which would be the better fuel on the basis of the heat

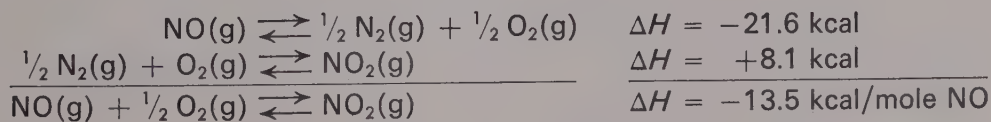
released per mole burned, nitric oxide, NO, or ammonia, NH_3 ? Assume the products are $\text{NO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$.

Answer

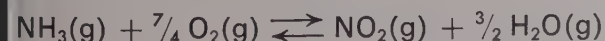
The burning of $\text{NO}(\text{g})$ can be shown by the equation



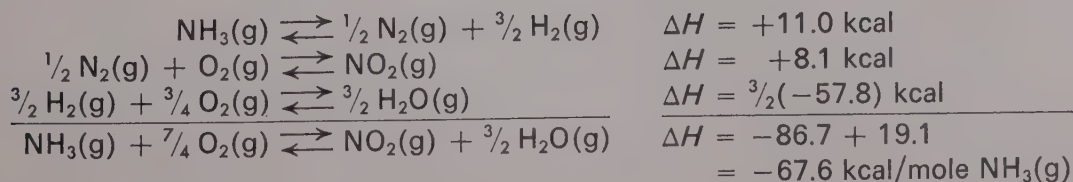
To find ΔH for this reaction, it is necessary to break the reaction down into steps for which ΔH is known.



The burning of $\text{NH}_3(\text{g})$ can be shown by the following equation:



This can be broken down into the following steps for which ΔH is known.

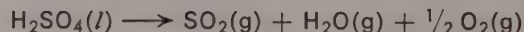


If the products of combustion of $\text{NH}_3(\text{g})$ are assumed to be $\text{NO}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$, the value of ΔH is -54.1 kcal/mole $\text{NH}_3(\text{g})$. The overall

conclusion is the same: $\text{NH}_3(\text{g})$ is the better fuel on the basis of energy per mole of fuel burned.

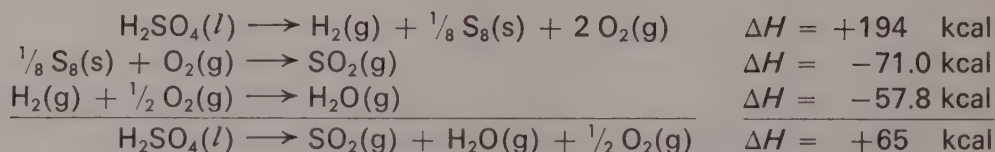
Problem 19

What is the minimum energy required to produce one mole of sulfur dioxide from sulfuric acid?



Answer. $\Delta H = +65$ kcal/mole $\text{SO}_2(\text{g})$.

Answer



To one mole of $\text{H}_2\text{SO}_4(\text{l})$ there must be added 65 kcal to make one mole of $\text{SO}_2(\text{g})$.

Problem 20

The heat of reaction for the formation of $\text{MgO}(\text{s})$ from the elements is -144 kcal/mole of $\text{MgO}(\text{s})$. How much

heat is liberated when magnesium reduces the carbon in CO_2 to free carbon? See Table 11-2.

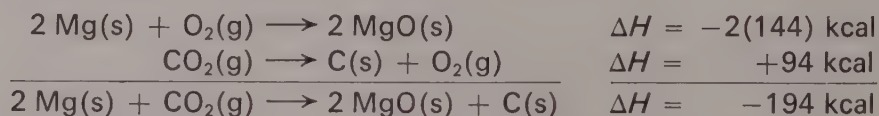
Answer. $\Delta H = -97$ kcal/mole MgO .

Answer

The overall reaction is:



This can be obtained as a result of the following reactions:



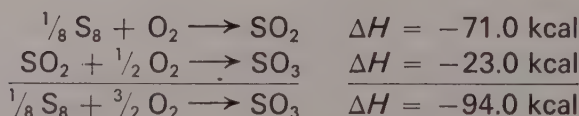
or $\Delta H = -97$ kcal/mole $\text{MgO}(\text{s})$

Problem 21

SO_2 can be combined with oxygen to give SO_3 . The

molar heat of reaction is -23.0 kcal/mole SO_2 . Calculate ΔH to form one mole of SO_3 from S_8 and O_2 .

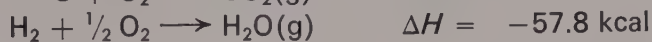
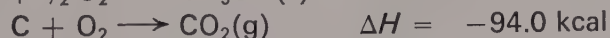
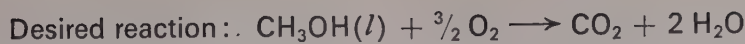
Answer



Problem 22

The formation of liquid methanol, CH_3OH , from elements

releases 152.6 kcal/mole CH_3OH . Calculate ΔH for combustion of one mole of methanol to CO_2 and H_2O .

Answer

Reversing the first equation, doubling the water equation, and adding gives the desired equation

$$\Delta H = 152.6 - 94.0 - 2(57.8) = -57.0 \text{ kcal}$$

Problem 23

How much water can be boiled by using the heat from completely burning one mole of carbon?

(a) If the water is at 100°C

(b) If it is at 0°C and must be warmed to 100°C first

Answer

$$(a) (\text{mass H}_2\text{O}) \left(\frac{\text{moles}}{\text{g}} \right) (\text{heat of vaporization/mole}) = \text{heat required}$$

$$(\text{mass H}_2\text{O}) \left(\frac{1 \text{ mole}}{18 \text{ g}} \right) \left(\frac{9.7 \text{ kcal}}{\text{mole}} \right) = (94.0 \text{ kcal})$$

$$\text{mass H}_2\text{O} = \frac{94.0 \times 18}{9.7} = 174 \text{ g}$$

$$(b) (\text{mass H}_2\text{O})(100^\circ\text{C})(1 \text{ cal/g-deg}) + (\text{mass H}_2\text{O}) \left(\frac{9700 \text{ cal}}{18 \text{ g}} \right) = 94.0 \times 10^3 \text{ cal}$$

$$(\text{mass H}_2\text{O})(100 + 540) = 94.0 \times 10^3$$

$$\text{mass H}_2\text{O} = 147 \text{ g}$$

The 9.7 kcal/mole value for vaporization at 100°C is not given in this chapter. The students will probably use 10.5 kcal/mole as given in Table 11-2. This larger ΔH will lead to these

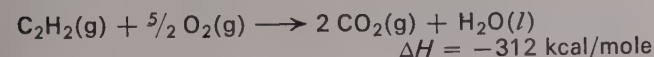
answers.

(a) 161 g

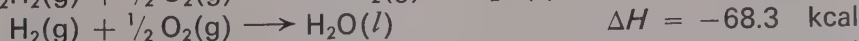
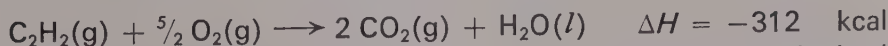
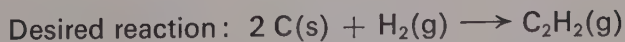
(b) 138 g

Problem 24

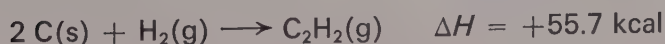
Combustion of acetylene, C_2H_2 , is represented by



What is ΔH for forming one mole of acetylene from carbon and hydrogen?

Answer

Reversing the first equation and adding gives



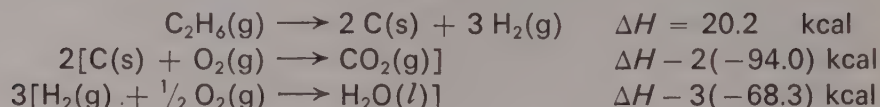
Problem 25

Which gives more heat on burning, a mole of acetylene

or a mole of ethane? See Problem 24 and Table 11-2 for data.

Answer

For ethane combustion the desired equation is



Adding gives the desired equation and

$$\Delta H = -372.7 \text{ kcal}$$

One mole ethane gives more heat than the 312 kcal liberated in burning one mole of acetylene (Prob. 24).

Note: In all problems that involve H_2O there is the possibility of discordant answers depending on whether the gas or liquid state is used. In this problem, liquid should be used to compare strictly with the acetylene. If the student assumes $\text{H}_2\text{O}(\text{g})$, he will find $\Delta H = -341.2 \text{ kcal}$, lower by three times the heat of condensation of water.

Problem 26

In Chapter 10, the family of saturated hydrocarbons was represented by the formula $\text{C}_n\text{H}_{2n+2}$. Each successive member of this family adds a $-\text{CH}_2-$ unit. Use the values in Table 11-2 and the equation



to estimate the ΔH for the formation of one mole of pentane, C_5H_{12} , from the elements. (Hint: calculate the change in ΔH for each additional CH_2 unit.)

Answer

	ΔH	difference per CH_2
CH_4	-17.9 kcal	
C_2H_6	-20.2	2.3 kcal
C_3H_8	-24.8	4.6
C_4H_{10}	-29.8	5.0

From the trend in ΔH values, we might expect the value for pentane to be about 5 kcal/mole greater than for butane. Estimated

$$\Delta H = -34.8 \text{ kcal/mole}$$

The experimental value is -35.0 kcal/mole .

Problem 27

Why is the Law of Conservation of Energy considered to be valid?

Answer

Because it "explains"—accurately correlates—a large amount of experimental data.

Problem 28

What do you think would happen in scientific circles if a clear-cut, well-verified exception was found to the Law of Conservation of Energy as stated in the text, page 201?

Answer

Either the law would be modified to fit the exception (plus all previous data) or it would be discarded and a new generalization sought. The same would be true for any other law.

Problem 29

Is energy conserved when a ball of mud is dropped from your hand to the ground? Explain your answer.

Answer

Yes, energy is conserved. The potential energy the mud had in your hand is converted into kinetic energy as the glob falls. When it hits the ground, the particles of mud are moved relative to each other. This movement requires energy and results in heating. Thus the potential energy is converted to heat.

Problem 30

List several things that can be done to a steel spring that will increase the energy stored in it.

Answer

Heat it.

Raise it above the base plane of reference.

Compress it.

Problem 31

What becomes of the energy supplied to water molecules as they are heated in a closed container from 25°C to 35°C?

Answer

The molecules move about more rapidly and rotate more quickly. The vibrations of the atoms within a particular molecule also increase, but only to a very small extent.

Problem 32

Outline the events and associated energy changes that occur on the molecular level when steam at 150°C and 1 atmosphere pressure loses energy continually until it finally becomes ice at -10°C.

Answer

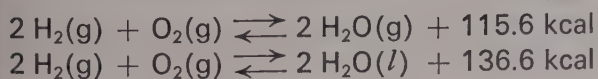
- (1) As the steam is cooled to 100°C the molecules slow down, hence their kinetic energy decreases. Moreover, the molecules rotate and vibrate less violently.
- (2) As the steam condenses to liquid water at 100°C, the molecules come much closer together, thus the potential energy decreases.
- (3) During cooling to 0°C (still liquid water) there is a decrease in kinetic energy.
- (4) The liquid water at 0°C freezes to ice at 0°C. The molecules lose some of their randomness. Their positions become fixed, such that their principal motion is one of vibration about a point. This is accompanied by a decrease of potential energy.
- (5) Finally, cooling the ice to -10°C decreases the kinetic energy of the system. The molecules vibrate less rapidly about their lattice positions.

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

Questions 1-3 relate to the following information found at 25°C.

Hydrogen gas and oxygen gas react according to the following equations:



1. How much more energy is stored in one mole of hydrogen molecules and $\frac{1}{2}$ mole of oxygen molecules than is stored in one mole of gaseous water molecules?

Answer: 57.8 kcal.

2. What is the ΔH for the formation of liquid water from hydrogen gas and oxygen gas?

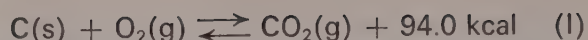
Answer: $\Delta H = -68.3 \text{ kcal/mole of H}_2\text{O}$.

3. Use the information given in the two equations to find the energy required to evaporate one mole of water, $\text{H}_2\text{O}(\text{l})$ at 25°C.

Answer: 10.5 kcal.

Questions 4-6 relate to the following information.

The two balanced equations are for reactions in which gaseous carbon dioxide is produced from the combustion of (I) solid carbon and (II) gaseous carbon monoxide.



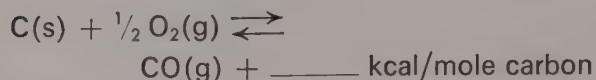
4. On the basis of the information given in equation (II), and assuming no change in temperature or pressure, one can correctly conclude that
- The rate of reaction is rapid.
 - The total number of moles of products is the same as the total number of moles of reactants.
 - The reaction is exothermic.
 - The mass of the product is greater than that of the reactants.
 - There will be an increase in the volume of the reactants and products taken together as the reaction proceeds.

Answer: c.

5. When 112 grams of carbon monoxide are consumed according to equation (II), which of the following occurs (molar masses: C = 12.0; O = 16.0 grams)?
- 1.0 mole of carbon dioxide is produced.
 - 67.6 kcal of heat are generated.
 - 2.0 moles of oxygen are consumed.
 - 0.25 mole of carbon dioxide is produced.
 - 0.50 mole of oxygen is consumed.

Answer: c.

6. On the basis of calculations using equations (I) and (II), find how much heat in kcal per mole of carbon would be produced in the following reaction.



- 20.6,
- 26.4,
- 41.2,
- 161.6,
- None of the above.

Answer: b.

7. It has been determined by calorimetric measurement that the complete fission of 500 grams of uranium yields about 10^{13} calories. The heat of combustion for 500 grams of coal is about 5×10^6 calories. Compare the amount of energy obtained when one kilogram of uranium undergoes fission to that obtained when one kilogram of coal burns.

Answer

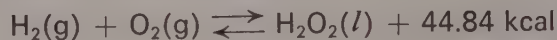
$$\frac{\text{energy fission}}{\text{energy burning}} = \frac{1 \times 10^{13} \text{ cal/500 g}}{5 \times 10^6 \text{ cal/500 g}} = 2 \times 10^6$$

8. When concentrated sulfuric acid is added to water, heat is liberated. The heat of dilution is about 18 kcal/mole of H_2SO_4 diluted with a large volume of water. Using the law of additivity of heat, predict how much heat would be released if 9.8 grams of H_2SO_4 were added to sufficient water such that all the heat of dilution would be released.

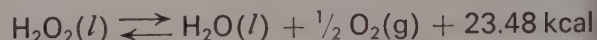
Answer

$$\frac{18 \text{ kcal}}{\text{mole}} \times \frac{1 \text{ mole}}{98 \text{ g}} \times 9.8 \text{ g H}_2\text{SO}_4 = 1.8 \text{ kcal}$$

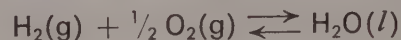
9. Given the two equations



and

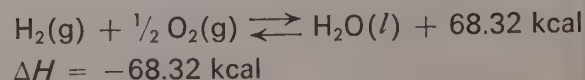


determine ΔH for

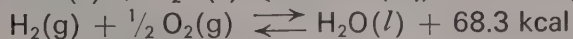
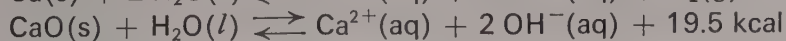


Answer

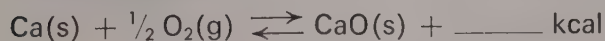
Add the two equations to obtain



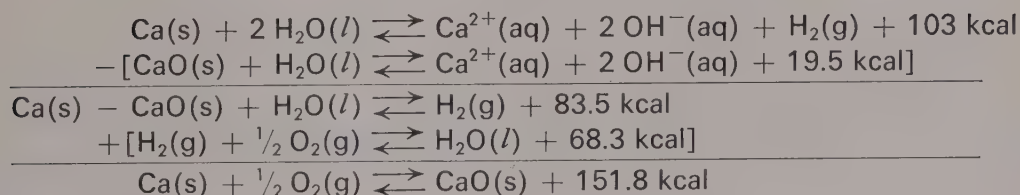
10. Given the three equations



Determine ΔH for

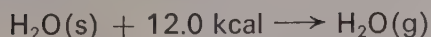


Answer



$$\Delta H = -151.8 \text{ kcal}$$

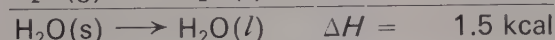
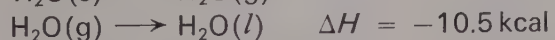
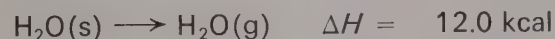
11. The sublimation of ice is shown by this equation.



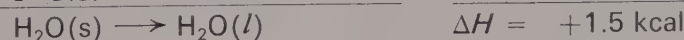
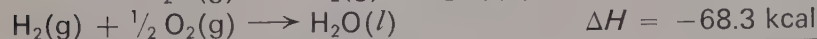
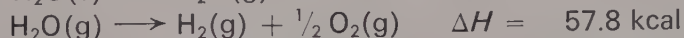
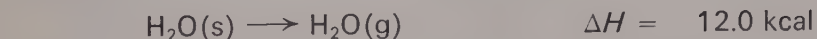
Calculate the heat of melting ice.

Answer

Desired equation: $\text{H}_2\text{O(s)} \longrightarrow \text{H}_2\text{O(l)}$

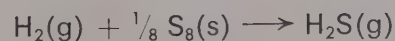
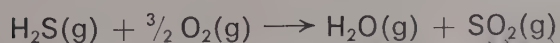


Another way to use the data from Table 11-2 is



12. H_2S can be burned according to the equation

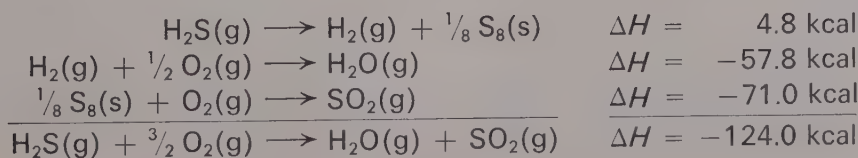
given that



Calculate the heat effect of this reaction,

$$\Delta H = -4.8 \text{ kcal}$$

Answer



The Rates of Chemical Reactions



Intent and Approach

Students will start this chapter with some idea that reactions proceed at different rates. However, you can expect they will have no idea of how to explain this or how to tie it to energy effects or the kinetic theory of gases.

This chapter will provide the explanation of reaction rate *via* the collision theory. This theory, combined with the kinetic theory of molecular motion, permits understanding how variation of concentration or temperature and adding a catalyst can change reaction rate. The heat of reaction is also integrated with the diagram used to show the activated complex. In addition to tying in some previous theories, the concepts introduced here will be used in the next chapter, on equilibrium.

Students are introduced to some of the principles of chemical kinetics (rate of reaction) by means of Experiment 28. The experiment permits the student to observe directly the effects of temperature and concentration on the rate of one set of chemical reactions.

It is important to remind the student that this is one of the frontiers in chemistry; that our understanding of reaction mechanisms is at best very limited; and that this is one of the exciting and important areas open to the able and interested chemistry student. In particular, the specific activated complex is known for only a very few reactions, and the exact mechanism is not available for many cases.

Outline

General comments; how rates are specified.

Factors affecting rates of chemical reactions are described.

How the nature of reactants influences the rate (12-1).

Collision theory is developed as a model for understanding the effect concentration has on reaction rate (12-2).

Reaction mechanism is explained and illustrated (12-3).

The collision theory, the temperature effect on reaction rate, the distribution of kinetic energies,

and the threshold energy for reaction are discussed (12-4).

Activation energy and the activated complex are introduced (12-5) along with the potential energy diagram to describe a reaction.

Heat of reaction is related to the potential energy diagram (12-6).

The action of catalysts is related to the activated complexes and potential energy diagram (12-7).

Further examples of mechanism (12-8) complete the chapter, except for a review (12-9).

SCHEDULE AND RELATED MATERIAL

Suggested Time : 10 days

Text Section	Topic and Other Work	Exercises	Problems		
			Easy	Medium	Hard
12-1	Demo. 28 Nature of Reactants		1, 2		
12-2	Expt. 28. Reaction Rates Concentration Effect <i>Film:</i> An Introduction to Reaction Kinetics	1, 2	4, 24	3, 25	
12-3	Reaction Mechanism	3	6, 7	5, 8	
12-4	Temperature Effect			9	10
12-5	Activation Energy		13, 19	12, 14-18	11, 20
12-6	Heat of Reaction			21	
12-7	Action of Catalysts <i>Film:</i> Catalysis		23	22	
12-8	More Mechanisms				
12-9	Review		28	26, 27, 29	30

New Concepts

1. Collision theory explains how reaction rates are changed by temperature and concentration.
2. Most reactions proceed by a series of reactions involving only two-particle collisions. The series is called the mechanism of the overall reaction.
3. Activation energy.
4. Distribution of kinetic energy values.
5. Catalysts influence the rate by providing a new, more favorable path for the reaction.

Development

INTRODUCTION

The student is probably aware that some reactions go rapidly and others more slowly, but any quantitative measure of this, or any explanation for it, will probably be new to him. The rate of reaction is very much like rate of travel—change in concentration/time compared to miles/time. The units used for concentration and time are chosen for convenience only.

Experiment 28 will introduce the student to both the qualitative and quantitative aspects of the factors which affect rates of chemical reac-

tions. The basic factors to be considered include the nature of the reactants, the temperature, and the concentration.

FACTORS AFFECTING REACTION RATES

12-1 The Nature of the Reactants

It may seem axiomatic that the nature of the reactant should have some influence on the rate and type of reaction. This section gives a rule of thumb for deciding on a rate. There is a buried point here that the student is not ready for as such—that is, to lay the basis for an ex-

planation of the generally slow rates with which organic substances react. The whole of organic chemistry would be different if organic reactions were quite rapid. Consider the number of compounds that will combine with oxygen but, at room temperature, do so at a rate so low that for practical purposes there is no reaction. These reactions are of the type that require bond breakage. As is true of any general statement, the rules given here and the above remarks apply to the majority of chemical changes, but not to every one.

In gaseous reactions, particularly at low pressure, reactions are sometimes slow if there is no third body to receive excess energy from the colliding molecules.

Expt. 28, A STUDY OF REACTION RATES,

fits here. See p. 140 in the Laboratory Guide.

**12-2 Effect of Concentration:
Collision Theory**

Collision theory is introduced as a model for describing chemical reactions and explaining reaction rates. Reactions occur as a result of collision between two particles. Hence it is reasonable that any change which increases the reactant concentrations gives more collisions per unit time and will increase reaction rate. For example, by increasing the pressure on a gas, by increasing the state of subdivision of reactants, and so on. Do not make a flat statement that a rise in concentration will give a greater rate. This rule does not always apply to the overall equations which are usually written. If we dealt with all the reactions of the mechanism, then the rate of each would be affected by concentration. It is best to use the concentration effect as a reasonable extension of collision theory, which turns out to be true many times and is understandable in terms of the reaction mechanism.

Film, AN INTRODUCTION TO REACTION KINETICS,

fits here. See p. 223 for summary.

12-3 Reaction Mechanism

Consider a very *complex* reaction involving the breaking, forming, and rearranging of numerous bonds. Such a reaction could not easily proceed at a favorable rate when you consider the necessity for collisions of numerous particles. Thus most complex reactions occur in a series of simple steps usually involving two-particle collisions. This series of reaction steps is called the mechanism of the reaction. Each step of the mechanism is governed by the same principles affecting rates of reaction that have been outlined earlier and each has its own potential energy curve involving its specific activation energy and its own activated complex. Note that the slowest reaction in the mechanism series becomes the "rate-determining step" for the entire reaction. Stress that the two following statements are good, general rules to remember. The reaction mechanism usually involves simple steps. The overall equation does not give the mechanism. The qualification in the first statement allows for slow reactions which could proceed at a low rate by complex steps. If a reaction is fast under normal conditions, it is safe to assume that the reaction involves simple steps. This statement does *not* say that all reactions have only simple steps.

As a corollary to the statements above, the kinetic behavior of a reaction is not (necessarily) given by the overall equation. Thus the study of kinetics has theoretical importance for understanding reactions, as well as practical value in revealing their speed.

**12-4 Effect of Temperature:
Collision Theory**

This section should be related to Section 4-6 (p. 66). The distribution of molecular velocities deduced there is now related to the rate of

DEVELOPMENT

reactions and their activation energy. Temperature changes cause large changes in the fraction of molecules that have high energies. In turn, the number of effective collisions per second is increased and a larger reaction rate is observed.

THE ROLE OF ENERGY IN REACTION RATES

12-5 Activation Energy

The bowling ball analogy is an easy introduction to the potential energy diagram. The latter is an important figure used to great advantage in describing the relationship between activation energy and rates of reaction. The activation energy is the minimum energy the colliding particles must acquire in order to bring about a chemical reaction. This is represented as an "energy barrier" which must be successfully overcome in order for a reaction to proceed.

You need to be careful in your language in discussing the energy required for formation of the activated complex. Avoid giving the impression that only the molecules having kinetic energy greater than E in Textbook Figure 12-5 can react. Such a statement is not true. Any molecule can react if it collides with a sufficiently energetic partner. The best way to convey this is to say that molecules having more than E energy are most likely to have fruitful collisions.

The transitory state of the reacting particles is called the *activated complex*. Here the reactants possess the required potential energy and may separate into original reactants or proceed to the products of the reaction. Use this model: a ball at the top of the hill can roll down either side. The activation energy may be thought of as the difference between the potential energy of the particle in the activated complex state and the potential energy possessed by the original, separated reactant molecules. Relatively little is known about the complex itself. It is some transitory combination of the reacting

atoms (molecules) in a state of high potential energy. Do not be drawn into a discussion of it.

The activation energy is not hard to determine, at least in theory. The Arrhenius equation relates reaction rate, k , to temperature, $^{\circ}\text{K}$, in this way:

$$2.303 \log k = -E_f/RT + \text{constant}$$

When k is measured at several temperatures, then a plot of $\log k$ versus $1/T$ usually gives a straight line of slope $-E_f/2.3R$.

The CHEM Study film "An Introduction to Reaction Kinetics" is very helpful for showing the activated complex and energy of activation. The first half is the most useful. The second half jumps from topic to topic rather rapidly and gets into catalysis—a subject better illustrated with the CHEM Study film "Catalysis." See page 223 for details of both films.

Figure 12-1 contains some sample potential energy diagrams that illustrate several types of reactions. Parts (A) and (B) are straightforward. Parts (C) and (D) are for the special cases in which E_f is so small that the reaction is spontaneous; that is, so many molecules (at a given temperature) have enough energy that most collisions are fruitful. Part (D) is useful to explain why there are few spontaneous endothermic reactions. The special relation shown by the diagram does not often occur.

Part (E) of the figure may be used at your discretion to illustrate a *hypothetical* diagram for an entire reaction mechanism. The three steps are analyzed in the caption and show one possible cause for a slow reaction (note the large E_f of the second step). This diagram, plus the section on reaction mechanism, should convince the student that there is much to learn about a reaction *and* that the overall equation, though quite useful, does not describe all aspects of the chemical change.

Part (E) of Figure 12-1 has a special pertinence because the HI decomposition example used in the Textbook is a combination of two diagrams combined as here.

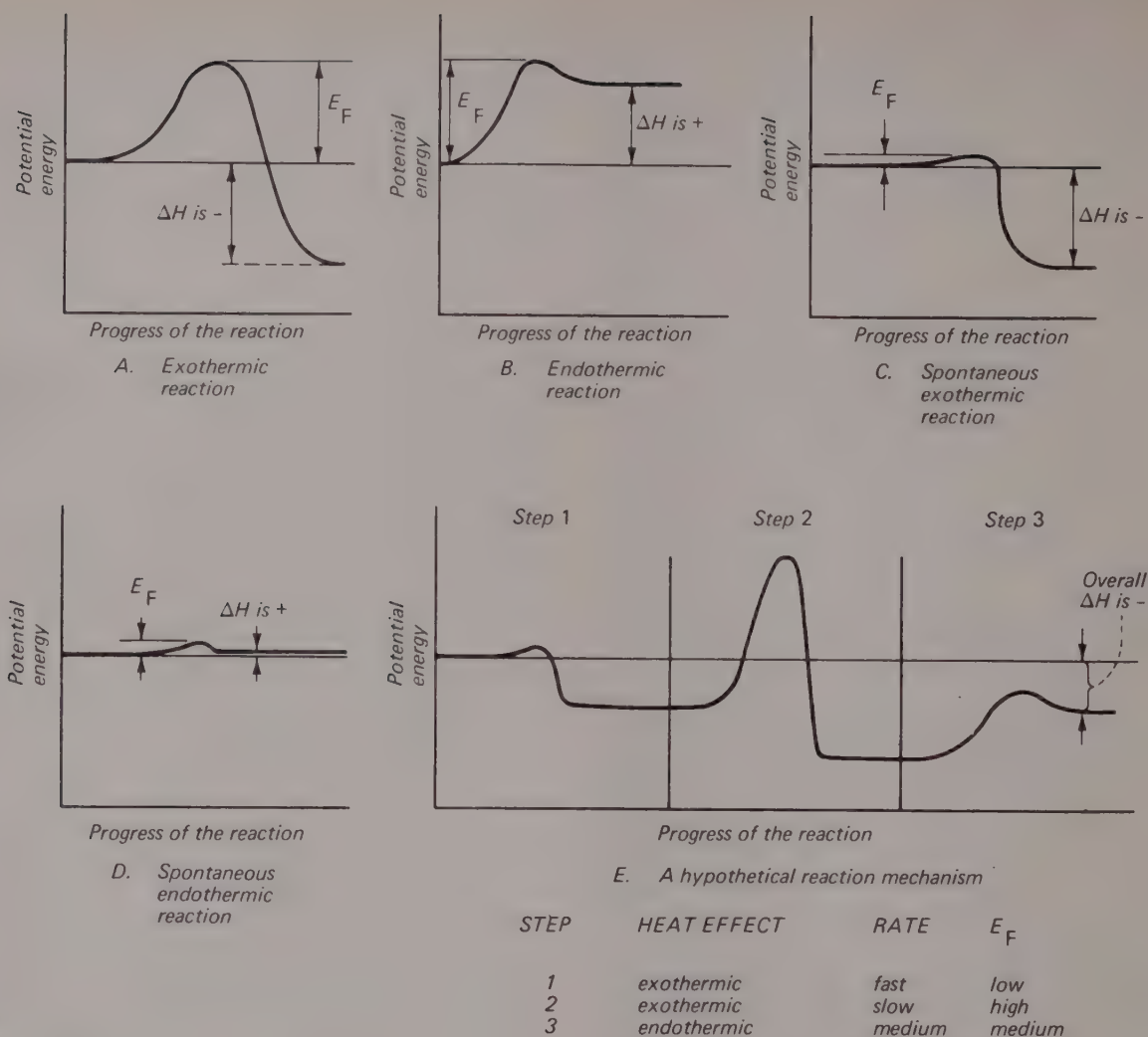


FIGURE 12-1

Some hypothetical potential energy diagrams.

12-6 Heat of Reaction

Use the potential energy diagram at this point to discuss endothermic versus exothermic reactions. Suggest the possible appearance of curves representing reactions which occur spontaneously. If the products of the reaction have a lower potential energy than the reactants, energy must have been released, and hence the reaction is exothermic (ΔH is negative). If the products of the reaction have a higher potential energy than the reactants, energy must have been absorbed, and the reaction is endothermic (ΔH is positive).

12-7 Action of Catalysts

There may be several possible reaction mechanisms for a chemical reaction, but one will always be the most favorable because it has the lowest activation energy. A catalyst provides a new path which is even more favorable because it has a still lower activation energy or produces a more favorable geometry, rendering more collisions effective. It is well to emphasize the fundamental property of catalysts at this point; they are substances which increase the rate but which are not permanently consumed by the reaction.

The bowling ball analogy is extended to

illustrate catalysis. The catalyst does not lower the activation energy of the uncatalyzed activation complex; it makes a *new activated complex* possible, and in this manner achieves the lower activation energy. The activated complex is *not* shown by the bowling ball model. The idea of different complexes will need emphasis in class.

Textbook Figure 12-13 is a new type of comparison between the molecular energy distribution curve and the activation energy curve. In the arrangement used the energy axes run parallel so that the student can see more easily the important relation between the fraction of high energy molecules and the activation energy.

Film, CATALYSIS,

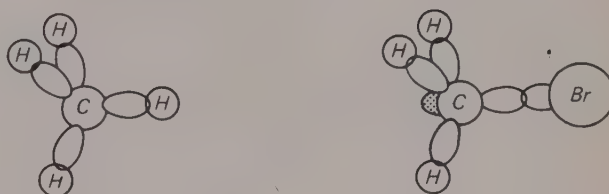
fits here. See p. 223 for summary.

12-8 Some Reaction Mechanisms

1. Molecular Inversion

Students may be puzzled by the reaction of CH_3Br and OH^- . Since CH_3Br is not ionized, why and how does OH^- attack it? Since all four of the available orbitals of carbon are filled in CH_3Br , how can OH^- form a bond to carbon before the carbon-bromine bond breaks?

The answer to this question is: in CH_3Br , the carbon-bromine bond has a certain degree of "ionic character"—that is, the electron-pair between C and Br is drawn closer to Br by virtue of the greater electronegativity of the halogen atom. This withdrawal of the electron-pair from carbon is equivalent to incomplete occupancy of one of carbon's four orbitals and permits the electron-pair of OH^- to take part in forming a weak bond to carbon. In methane, C—H bonds are of such a character that no electron deficiency exists on carbon, thus there are no "unoccupied" orbitals. These molecules are illustrated below.



Since one carbon orbital in CH_3Br is not fully occupied, electrons of an approaching reagent can overlap at the side of the carbon atom opposite the direction of the C—Br bond. Thus the reaction with HO^- can be pictured as in Figure 12-2.

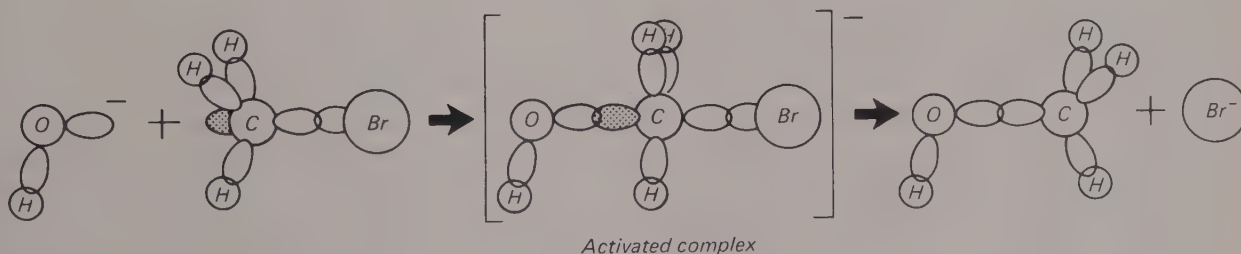


FIGURE 12-2

Schematic mechanism of the reaction $\text{CH}_3\text{Br} + \text{OH}^- \rightleftharpoons \text{CH}_3\text{OH} + \text{Br}^-$.

A consequence of the reaction according to this scheme is that the attacking reagent becomes attached to the side of the carbon atom opposite that at which the displaced group was bonded. The configuration of the groups around the carbon atom becomes inverted in the process.

(Note: Compare Textbook Figure 12-14 with these sketches.)

There is a further discussion of this reaction in the article by J. D. Roberts, "Organic chemical reactions," *Scientific American*, November 1957, p. 117.

2. Chain Reactions

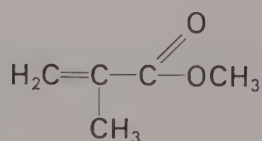
Chain reactions are important in many polymerizations. Polyethylene, well known to students, is made by such a process. Tygon tubing is a copolymer of vinyl chloride, $\text{H}_2\text{C} = \text{CHCl}$, and butyl phthalate joined by a chain-reaction mechanism.

3. Acid Catalysis

Catalysis by H^+ is a very important process. A simple example has been chosen for the text. The formic acid example (Textbook Figures 12-15 and 16) illustrates the point fully.

In the formic acid example, we mention the hydrogen ion, H^+ . You will see that when we discuss acids (Chapter 14) we use H_3O^+ . The point is that we do not want to give the justifications for the hydrated form here in the chapter on rates. Make no special point about *either* representation now; let the argument develop in Chapter 14. In the film, "Catalysis," the proton will be shown as a part of a sulfuric acid molecule, H_2SO_4 . This is appropriate because the film shows the reaction in pure formic acid, where undissociated sulfuric acid molecules are present.

Lucite and Plexiglas are made by polymerizing methylmethacrylate,



This monomer is made from acetone by an acid catalyzed process.

4. Other Catalysts

In many catalysts of practical importance, a complex is formed as a result of some interaction with special sites on a solid surface of metal or oxide (usually SiO_2 , Al_2O_3 , or $\text{SiO}_2\text{-Al}_2\text{O}_3$ mixtures). In principle these examples are similar to that given for formic acid,—but they are complicated and not well understood.

Many industrial processes use solid catalysts.

Some of them are

ammonia synthesis	iron catalyst
H_2SO_4 manufacture	Pt
cracking petroleum fractions	$\text{SiO}_2\text{-Al}_2\text{O}_3$
reforming petroleum fractions— to make isomers with higher octane numbers	Pt on $\text{SiO}_2\text{-Al}_2\text{O}_3$

Occasionally the term "negative catalyst" is used. This is a poor phrase for the following reasons. It implies the existence of a substance (not consumed in the reaction) which slows down a reaction. This, in turn, would mean an activated complex of *higher* activation energy than for the uncatalyzed reaction. But molecules do not pick their path for scenery; the lowest energy route is most used. Thus the regular reaction would occur along with a few high energy cases that might proceed over the higher energy barrier. The net effect of the higher path could *only* be to speed up the reaction.

There are substances which can cause a reaction to go more slowly. But the change in rate is caused by the substance reacting (*and being consumed*) while removing a needed reactant or catalyst. The lowered concentration of the reactant, or loss of catalyst, leads to a lower rate. For example, sodium hydroxide will reduce the rate of formic acid decomposition by consuming the catalyst, H^+ .

A more dramatic example is the commercial reaction in which large hydrocarbon molecules are broken (cracked) and hydrogen is added. The process uses a platinum catalyst in the form of very small pieces (a few hundred Å in diameter), which provide a large surface area. Sulfur reacts with the surface and, in effect, removes it. For all practical purposes, the reaction stops after the addition of a minute amount of sulfur, which is called a "poison" for the catalyst.

12-9 Review

Supplementary Material

Book

E. L. King, *HOW CHEMICAL REACTIONS OCCUR*, W. A. Benjamin, Inc., New York (1964). A paperback dealing with all the topics of this chapter. Equilibrium is also covered.

Article

Chemistry **40**, April, p. 29 (1967) has a discussion of the $I_2 + H_2 \rightleftharpoons 2 HI$ reaction.

Films

For ordering information see the *List of Film Sources* at the back of the Teacher's Guide.

AN INTRODUCTION TO REACTION KINETICS

A CHEM Study film

Running Time: 13 minutes

This film was prepared in collaboration with Dr. Henry Eyring. It treats the reactions of Cl_2 and I_2 with H_2 ; touching on mechanism, activation energy, collision geometry, reversibility and equilibrium (10 minutes). The last

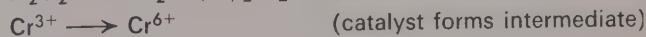
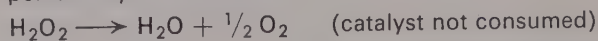
few minutes deal more sketchily with catalysis and the effect of temperature and pressure. The film is good enough to show twice: the first time as an introduction; the second time, after Chapter 12 has been covered. If only one showing is planned, schedule it late in the chapter. See comments (p. 228) on the small fraction of effective collisions.

CATALYSIS

A CHEM Study film

Running Time: 17 minutes

This film, prepared in collaboration with Dr. R. E. Powell, treats five examples of catalysis. The second, formic acid decomposition, is particularly well related to the text (pp. 220–222). The other four reactions and the points they illustrate are:



Good use is made of potential energy diagrams.

Background Discussion

In Chapter 11 you discussed how to find the energy balance of a chemical reaction—both how to measure it and how to compute it. You also pointed out some possible ways in which energy can be stored in a molecule. In Chapter 12 you will be concerned with the rates of chemical reactions. You may wonder why this great emphasis on reaction rates, especially since this subject has been of little concern in the high school chemistry course. If you have doubts about the wisdom of such an approach, consider the ultimate goal of the chemists—i.e., the prediction of the conditions that induce chemical reaction. The chemist is concerned with three basic questions: Can reaction occur? How long will it take? How far will the reaction proceed?

In Chapter 11 the point was made that many reactions occur with the evolution of heat. For some of these (the reaction of NO with O_2), all that is required is to bring the reactants

together; for others (the reaction of H_2 with O_2), the reactants must be heated or ignited by a spark. What is responsible for the great difference in the rate of these two exothermic reactions? This problem will be explored in some detail in this chapter. It can be pointed out now, however, that many reactions, even exothermic ones, require an input of energy to start them. This "starting" energy is released as the reaction proceeds. Endothermic reactions require more energy than is actually consumed when the reaction occurs. Since the energy required to initiate reaction is not absorbed in the reaction, it is called *activation energy*. Reaction rates and activation energy form the subject matter of this chapter.

The emphasis we place on activation energy and reaction rates does not result from our great knowledge of these properties at the present time—indeed, much of our knowledge of reac-

tion rates is still obtained by purely empirical methods—but rather from the recognition that one of the most important unsolved problems in chemistry is the accurate prediction of reaction rates. By presenting chemistry from this point of view you are involving the beginning student in the really significant problems of modern chemistry.

The following topics are discussed:

Reaction Rates: Ways to Measure

Reaction Rates: Order of Reaction and Reaction Rate Constants

Activation Energy

The Distribution Curve

Factors Affecting Reaction Rates

Reaction Mechanism

The Mechanism of the Hydrogen-Iodine Reaction

Catalysis

Reaction Rates: Ways to Measure

Reaction rates are determined by measuring the rate at which some property of the reaction changes. Among the properties which have been studied are color, volume of the system, pressure, index of refraction, rotation of polarized light, mass of precipitate produced, and pH. The examples in Table 12-1 illustrate how some of these properties are applied. The reactions are for illustration only; not to be studied in detail.

TABLE 12-1

Illustrative Examples of Properties Used to Follow Reaction Rates

<i>Property Changing</i>	<i>Sample Reaction</i>
color	$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$
volume	$\text{N}_2\text{O}_5(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$
pressure	$\text{H}_2\text{O}_2(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{l}) + \frac{1}{2} \text{O}_2(\text{g})$
rotation of polarized light	$\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$ sucrose glucose fructose
absorption of light	$\text{Eu}^{2+}(\text{aq}) + \text{H}^+(\text{aq}) \rightleftharpoons \text{Eu}^{3+}(\text{aq}) + \frac{1}{2} \text{H}_2(\text{g})$ europium(II) europium(III) (colorless) (pink-red)
mass	$\text{Ag}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{CH}_3\text{I}(\text{aq}) \rightleftharpoons \text{AgI}(\text{s}) + \text{CH}_3\text{NO}_3(\text{aq})$ methyl iodide methyl nitrate
pH	$(\text{C}_2\text{H}_5)_2\text{O}(\text{aq}) + \text{HI}(\text{aq}) \rightleftharpoons \text{C}_2\text{H}_5\text{I}(\text{aq}) + \text{C}_2\text{H}_5\text{OH}(\text{aq})$ ethyl ether ethyl iodide ethanol

Reaction Rates: Order of Reaction and Reaction Rate Constants

An examination of the graph plotted in Experiment 28 shows that the rate of that overall reaction depends on the concentration of the reactants. The student may inquire about the concentration at which the rate should be measured and about how reaction rate can be tied to a particular reaction. This will give you an opportunity to use some quantitative equations. Suppose the reaction of interest is given by the equation



A quantitative definition of the rate of this reaction is

$$\frac{-\Delta[\text{N}_2\text{O}_5]}{\Delta t} \quad (2)$$

which is read: the change in concentration of dinitrogen pentoxide with change in time. The minus sign shows that N_2O_5 is a reactant and is used up as time goes on. The brackets indicate concentration, often expressed in atmo-

BACKGROUND DISCUSSION

spheres for gases. Since the value of the ratio in expression (2) will depend on the time over which it is measured, it is customary to define the reaction rate for an extremely short interval of time and write it as

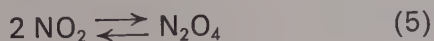
$$\frac{-d[\text{N}_2\text{O}_5]}{dt} \quad (3)$$

Since experiments show that the rate of this reaction is directly proportional to $[\text{N}_2\text{O}_5]$, we can write

$$\frac{-d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5] \quad (4)$$

where k is a constant that is characteristic of the reaction under study. It is called the *reaction rate constant*, and defines the fraction of N_2O_5 that reacts per unit of time. In a first-order reaction the *fraction* which reacts per second is independent of the particular concentration of N_2O_5 . Equation (4) contains only first degree terms; it is said to define a *first-order reaction*.

The rate of the reaction



is expressed by the equation

$$\frac{-d[\text{NO}_2]}{dt} = k[\text{NO}_2]^2 \quad (6)$$

The rate of this reaction depends on the square of the concentration of the reactant, and since this rate equation is of the second degree, the reaction is defined as second-order.

Reaction rate constants are computed from the kind of data obtained in Experiment 28; i.e., concentration-time data. To do this it is convenient to change the form of equations (4) and (6) by integrating. Equation (4) yields

$$\ln [\text{N}_2\text{O}_5] = -kt + \ln [\text{N}_2\text{O}_5]_0 \quad (7)$$

where $[\text{N}_2\text{O}_5]_0$ is the initial concentration of N_2O_5 at $t = \text{zero}$. The abbreviation, $\ln$, means natural logarithm ($\ln = 2.303$ logarithm to the base 10). Observe that equation (7) is of the form $y = mx + b$, the plot of which is a straight line. Sample plots of some rate data for a first-

order reaction are shown in Figure 12-3. In Figure 12-3A, the data are plotted as they were in Experiment 28. In Figure 12-3B, the logarithm (base 10) of the concentration is plotted against time. The slope of the line is equal to $-k/2.3$, hence k can be computed readily.

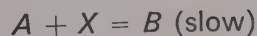
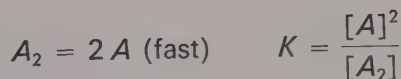
In a similar manner equation (6) can be integrated to give

$$\frac{1}{[\text{NO}_2]} = +kt + \frac{1}{[\text{NO}_2]_0} \quad (8)$$

which also is of the form $y = mx + b$. A plot of $1/[\text{NO}_2]$ against time will produce a straight line with a slope equal to $+k$, giving the rate constant of a second-order reaction. It should be possible to use the techniques discussed above to show the more inquisitive students how rate constants are obtained.

The product of the exponents of the concentration terms in a rate equation may not be an integer, but fractional or zero. In these cases the order of the reaction is said to be fractional or zero. There is nothing special about a fractional-order reaction.

Fractional orders arise from successive reactions. Here is a general case. The equilibrium constant is shown by K and the rate constant by k .



$$\frac{-d[\text{X}]}{dt} = k[\text{A}][\text{X}]$$

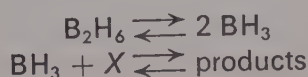
But, from the first reaction,

$$[\text{A}] = \sqrt{K[\text{A}_2]}$$

hence

$$\frac{-d[\text{X}]}{dt} = k\sqrt{K}[\text{A}_2]^{1/2}[\text{X}]$$

A specific example is diborane,



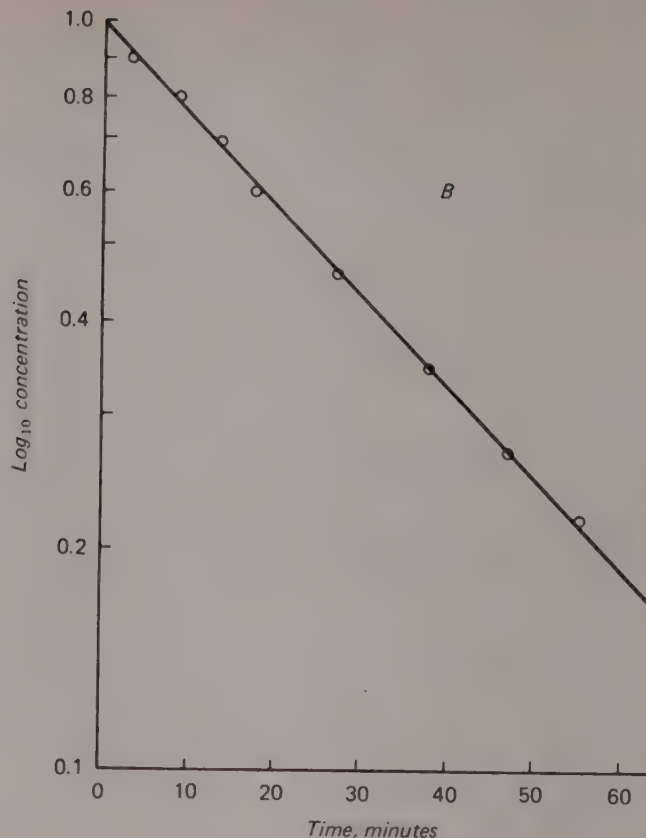
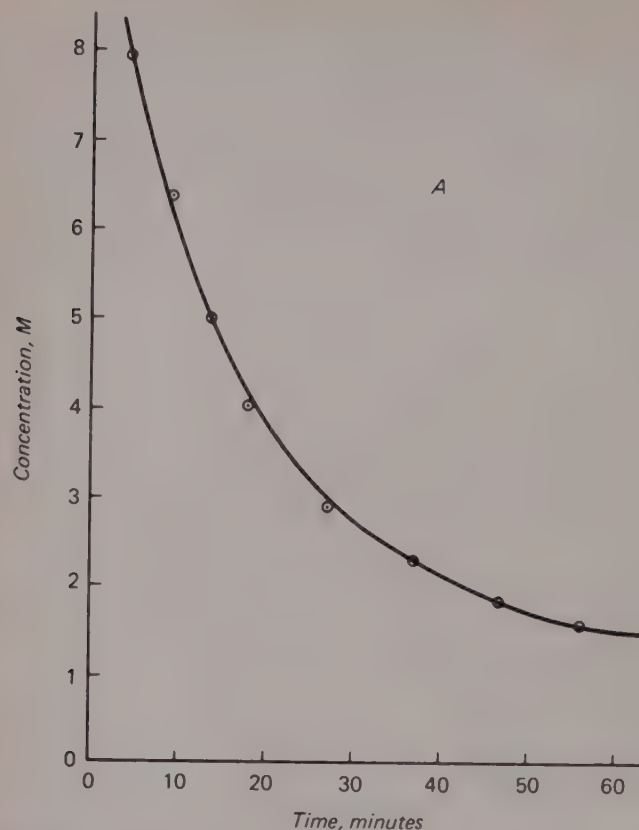


FIGURE 12-3

Two ways to plot the same rate data.

The various k 's for the different orders of reaction have different units. They are shown below.

Order	k	Units (conc. in moles/liter)
0	k_0	moles/liter/sec
1	k_1	sec^{-1}
2	k_2	$\text{liter mole}^{-1} \text{ second}^{-1}$
$\vdots$	$\vdots$	$\vdots$
n	k_n	$\text{liter}^{n-1} \text{ mole}^{1-n} \text{ second}^{-1}$

Activation Energy

We commented about activation energy in the section on philosophy. You should discuss this in some detail in your lectures. Many students will want to know more about it, such as: How is it measured? Can it be calculated? What does it mean? Activation energies can be calculated for some very simple reaction such

as $\text{H}^* + \text{H}-\text{H} \rightleftharpoons \text{H}-\text{H}^* + \text{H}$ (the asterisk is used here merely to label one of the hydrogen atoms). Such calculations involve the use of quantum mechanics, which is beyond our level of mastery at this time. On the other hand, an understanding of how activation energies are measured can be grasped by your more alert students. In Experiment 28 the student studied the way in which the rate of a reaction varied with temperature. Such data could be used to compute specific reaction rates at various temperatures. It has been shown experimentally that the variation of the specific reaction rate with temperature is given by the equation

$$\frac{d(\ln k)}{dT} = \frac{E_F}{RT^2} \quad (9)$$

where $\ln = 2.303 \log_{10}$, E_F = activation energy, T = absolute temperature, and R = the gas constant ($1.99 \text{ cal mole}^{-1} \text{ deg}^{-1}$). Integration of

equation (9) yields

$$\log_{10} k = \frac{-E_F}{2.3R} \left(\frac{1}{T} \right) + B \quad (10)$$

where B is a constant. Here again, when $\log_{10} k$ is plotted against $1/T$, a straight line is obtained that has the slope

$$-\frac{E_F}{2.3R}$$

The activation energy can then be evaluated from the slope of this line. Activation energies have been evaluated in this way for a number of reactions, and have values ranging from 1 to 100 kcal/mole. High activation energies are associated with slow reaction rates.

Rewriting equation (10) to express the difference in reaction rates at the temperatures T_1 and T_2 yields

$$2.3 \log_{10} \frac{k_1}{k_2} = -\frac{E_F}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (11)$$

You have probably heard the expression that "a 10 C° rise in temperature will about double the rate of reaction." Let us investigate this statement. By setting $k_2 = 2k_1$ and $T_2 = T_1 + 10$, we can find from equation (11) that for this statement to be true at room temperature, E_F must be about 15 kcal/mole. The derivation of equation (11) includes the assumption that E_F is constant with temperature change.

Immediately we see two difficulties with this rule of thumb. First, the rule can't fit except over a small range near room temperature. For instance, the change in rate from 325°C to 335°C for such a reaction would be only 20%. At -125°C a rise of 10 C° would make a *28-fold increase in rate!* Second, not all (or even most) reactions oblige by having $E_F = 15$ kcal/mole.

You can still make use of the expression by saying that sometimes it is true and that this illustrates how big the temperature effect can be. Only the better students need be told that, for the reasons given above, the effect can be either greater or less.

These results are more supporting evidence that molecules with energy in excess of a certain

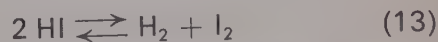
minimum energy are most likely to react. Reference to Figure 12-2 in the Textbook shows that a small increase in temperature does not greatly increase the average kinetic energy of the molecules. If reaction occurred mainly among molecules with average kinetic energy, such a small increase of temperature could not produce a marked effect on reaction rate. The marked change of rate of some reactions with a rise in temperature is just what would be expected if molecules with energy greater than E of Figure 12-2 are reacting; for it is the number of these high energy molecules which increases so rapidly with temperature.

The Distribution Curve

Support for the view that only a certain fraction of the molecules of a system possess sufficient energy to make reaction probable when they collide is obtained from a computation of the number of collisions in a molecular system. An equation (developed from kinetic molecular theory) for computing the number of collisions between like molecules is

$$Z = \frac{1}{2} \sqrt{2} \pi n^2 d^2 \sqrt{\frac{8kT}{\pi m}} = 2n^2 d^2 \sqrt{\frac{\pi kT}{m}} \quad (12)$$

where n is the number of molecules per cubic centimeter, d is the molecular diameter, and $\sqrt{8kT/\pi m}$ is the average speed of a molecule of mass m . Solution of equation (12) shows that HI molecules at 280°C and a concentration of 1 mole/liter collide about 6×10^{31} times per second per cubic centimeter. However, reacting in accordance with the equation



H_2 is produced at a rate of only about 2×10^{14} molecules per second per cubic centimeter, which means that only three in about 10^{18} collisions are effective in producing reaction. Apparently, molecules must acquire a certain critical energy before they can react. This energy is that which the reactants must acquire to mount the potential energy hill shown in Figure 12-5 of the Textbook.

The large proportion of ineffective collisions is *not* brought out in the film "An Introduction to Reaction Kinetics" for this reason: it would be impractical to draw 10^{18} collisions to show just three fruitful ones. You can prevent a wrong impression of the relative frequency of reaction by commenting on this mechanical limitation.

Factors Affecting Reaction Rates

We have assumed that molecules will not react unless they possess the necessary activation energy. The student may inquire whether all such molecules react when they collide. To answer this question you need to know the number of molecules that possess the necessary activation energy. An approximation of this number can be obtained from the exponential form of equation (9), which is

$$k = Ae^{-E_f/RT} \quad (14)$$

This equation was defined first by Arrhenius. The factor $e^{-E_f/RT}$ defines the fraction of molecules which possess the necessary energy to react. In terms of the simple collision theory presented in the Textbook (Secs. 12-2 to 12-4) the reaction rate, k , ought to equal the product of the total number of molecular collisions and the fraction, $e^{-E_f/RT}$, of these collisions that possess the required activation energy, E_f . If this statement were true, A in equation (14) would merely be the number of molecular collisions. This simple model applies satisfactorily for a few gaseous reactions. Using this simple view of A and the measured value of E_f for the decomposition of HI we can calculate k to be 2.10×10^{-3} liter mole $^{-1}$ sec $^{-1}$ at 700°K. The experimental value is 1.57×10^{-3} . For most chemical reactions, however, the rate calculated on the basis of this model is much larger than the experimental rate.

The simple model presented in the Textbook assumes hard elastic spheres which can collide with free transfer of kinetic energy. If a molecule is struck by another molecule having the proper energy, a reaction should occur, and reaction rates computed on the basis of this simple model should agree with measured reaction rates. The

failure of agreement must mean that our simple model is not completely correct.

That such a simple model does not reproduce the behavior of more complicated molecules really is not surprising, for molecules involved in such reactions may contain a number of bonds, only one of which is broken in a particular reaction. For reaction to take place, the collision must occur such that most of the energy is imparted to the bond to be broken; i.e., the molecules must collide with the proper orientation. The requirement that molecules collide at a certain spatial orientation for maximum chance of reaction is called *collision geometry*. It has been suggested that equation (14) be written

$$k = pZe^{-E_f/RT} \quad (15)$$

where p , the steric factor, measures the geometrical requirement and Z , the frequency factor, measures the collision number. See page 255 for further discussion of Arrhenius' equation.

The spatial orientation most conducive for chemical reaction may represent an orientation which has a high potential energy for the approach of the reactant molecules. Owing both to ionic charges and to those resulting from permanent and induced dipoles, molecules tend to approach each other in certain preferred orientations. Further, two molecules may collide with sufficient energy to react and yet not do so because vibrational energy is quantized and because the energy cannot be transferred in the proper size quantum. *The molecular species formed when molecules collide with sufficient energy to react is called an activated complex.* Even the formation of such a complex does not insure reaction, for the complex has some probability of decomposing to re-form the reactants rather than the products. The answer to the student's question, then, is that molecules with sufficient activation energy definitely may collide without reacting. One conclusion from the foregoing discussion is that in all reactions, endothermic as well as exothermic, the activated complex always decomposes with the liberation of energy.

BACKGROUND DISCUSSION

Reaction Mechanisms

The beginning student is apt to assume that chemical equations define the mechanism by which a reaction proceeds; i.e., the number of molecules of reactants written in the equation must collide simultaneously in order to form the products. Although this is true of some reactions, it is not true for most. For example, in the decomposition of HI, equation (13), two molecules of HI collide and produce H_2 and I_2 . In the reaction of Fe^{2+} and MnO_4^- , five Fe^{2+} and eight H^+ do not collide with a MnO_4^- ion simultaneously. Indeed, as pointed out in the text, even a three-body collision is rare. Complex reactions are believed to occur in a series of simple steps. The mechanism of a reaction is derived from a study of reaction rates. Some examples will be given to illustrate how this is done.

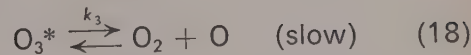
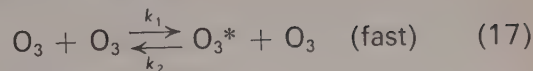
We have assumed that molecules must collide to react. For the decomposition of HI this means that two molecules must collide to form H_2 and I_2 . Thus the rate of this reaction would be expected to be given by the equation

$$\frac{-d[HI]}{dt} = k[HI]^2 \quad (16)$$

Experimentally the rate of this reaction does fit this second-order rate equation. Such a reaction is said to be bimolecular; i.e., the actual mechanism involves the collision of two molecules.

According to collision theory, all reactions should be at least bimolecular, since at least two molecules must collide for any reaction to occur. However, the decomposition of N_2O_5 , equation (1), and a number of other reactions are known to follow the first-order rate law (equation 4). How can the order of such reactions be explained in terms of collision theory? It is quite probable that even a first-order chemical reaction is bimolecular and does not involve simply the decomposition of a molecule, although there are many reactions whose rates are defined quite well by the first-order rate law. The decomposition of ozone is such a reaction. A possible mechanism for this reaction is given by

the series of equations



The rate of formation of oxygen is controlled by the slow decomposition of activated ozone, O_3^* , shown in equation (18) and can be written

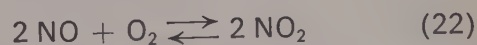
$$\frac{d[O_2]}{dt} = k_3[O_3^*] \quad (20)$$

Note that $d[O_2]/dt$ is positive because O_2 is a product and is being *formed* as time goes on. Reaction (17) is reversible, and at equilibrium under relatively high pressures the concentration of the activated molecules remains fairly constant:

$$\frac{[O_3^*]}{[O_3]} = \frac{k_1}{k_2} = K_e \quad (21)$$

Therefore the rate of decomposition of ozone appears to be first-order even though it involves some bimolecular collisions.

Trimolecular reactions are possible but rather rare. This is true because three-body collisions are rather infrequent. An example of a trimolecular reaction which follows the third-order rate law is



The rate of this reaction is given by the equation

$$\frac{-d[NO]}{dt} = k[NO]^2[O_2] \quad (23)$$

The Mechanism of the Hydrogen-Iodine Reaction

You may wonder at our treatment of the hydrogen-iodine reaction because it is different from that in most textbooks. Early in 1967, J. H. Sullivan published the results of a set of experiments that are more satisfactorily explained by a different mechanism. See *J. Chem. Phys.* **46**, 75 (1967). Let us see what the situation was and then consider Sullivan's interpretations.

The rate constant for a chemical reaction depends on temperature according to the Arrhenius equation (14), page 228. Plotting $\log k$ vs $1/T$ gives a straight line with slope $-E_F/2.3R$ as in equation (10). Figure 12-4 shows Sullivan's

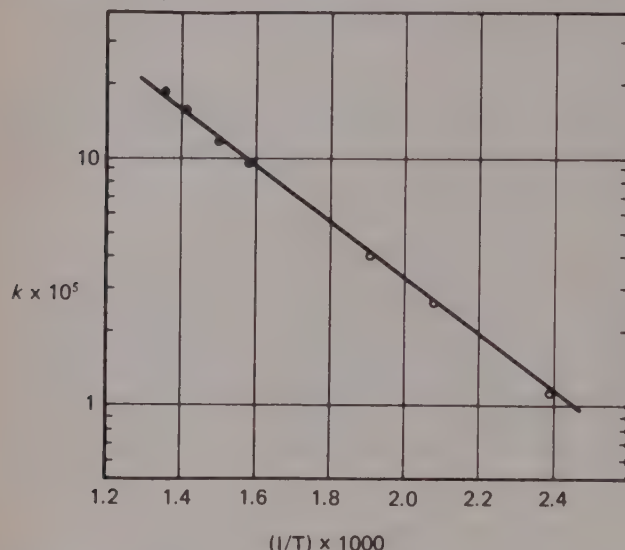


FIGURE 12-4

Arrhenius plot for $H_2 - I_2$ reaction.

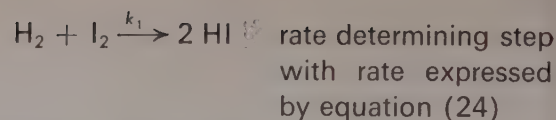
data plotted in this fashion. The solid dots show results taken in the same manner used by Bodenstein in his classical work done in 1894-97. It is this work that is usually quoted. Relatively high temperatures (556-781°K) were required because the rate of the reaction is low at room temperature.

Bodenstein found that his experiments agreed with this rate expression

$$\text{Rate} = \frac{d[HI]}{dt} = k[H_2][I_2] \quad (24)$$

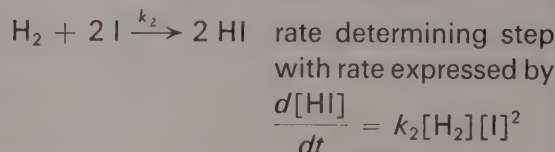
Chemists have long recognized that several different mechanisms could lead to this rate expression but there seemed no way to decide which one was correct. The dilemma is that the two most likely mechanisms are connected, in a sense, by the equilibrium dissociation of iodine molecules into atoms. The following sets of equations show the situation.

For the direct reaction of molecules



The simplest interpretation suggests that the slowest step in the reaction involves the collision of one hydrogen molecule with one iodine molecule.

For the reaction of atoms (the atomic mechanism)



In this interpretation, the slow step involves a ternary collision between one hydrogen molecule and two iodine atoms. The dissociation of iodine into atomic iodine allows us to change the appearance of this equation since

$$[I]^2 = K[I_2]$$

Therefore

$$\begin{aligned} \frac{d[HI]}{dt} &= k_2 K [H_2][I_2] \\ &= k_1 [H_2][I_2] \end{aligned}$$

Sullivan showed how to resolve this problem by generating atomic iodine by photochemical methods. This means that the rate controlling step can be studied at relatively low temperatures. Sullivan used light (5780 Å) to decompose I_2 into I atoms. In the presence of H_2 , he found the rate of formation of HI to be proportional to $[I]^2$ and not $[I]$. The open circles in Figure 12-4 show these results. The fact that these values fall on the same straight line as those produced by Bodenstein's method (the dots), means that the constants of Arrhenius' equation is the same for both sets of data. This provides strong support for the atomic mechanism given above rather than the molecular mechanism, which had been accepted for over fifty years.

Sullivan also showed that the chain reaction mechanism that applies to the H_2-Cl_2 and H_2-Br_2 reactions is not applicable to the H_2-I_2 reaction. The chain mechanism would probably

require the rate of HI formation to be proportional to $[I]$.

You should not try to discuss these arguments with your class. However you might want to point out that this example is similar to the discovery that noble gases can form compounds. For the H_2-I_2 reaction, the scientific community must now discard the molecular mechanism and accept the atomic one *because new experiments have been carried out that cannot be explained by the molecular mechanism*. There is a discussion of this development in *Chemistry*, **40**, 29 (1967) under the title "Bewhiskered Theory Disproved."

Catalysis

We have postulated that a catalyst functions by providing a new reaction path with lower activation energy (Textbook Figure 12-12). Some students may want to know more about the mechanism by which a catalyst works. Some possible ways that the faster reaction may be achieved are by (a) promoting the formation of a new activated complex; (b) providing a path by which energy can be transferred in small steps; or (c) promoting the optimum geometry. Two broad classes of catalysts are recognized—heterogeneous catalysts and homogeneous catalysts. Heterogeneous catalysts are usually solids having a very large surface area, either finely divided, such as platinum black, or quite porous,

such as activated charcoal.

A heterogeneous catalyst (a two-phase system; often gaseous reactants on a solid catalyst) may be pictured as having a large number of molecules on the surface. Molecules in the body of the material have their binding forces neutralized in all directions. Surface molecules have unusual properties because of their incompletely satisfied bonding possibilities. When a dipolar molecule such as HI strikes such a surface in just the right way, it will adhere. Its vibrations will be altered by the catalyst, and it probably receives sufficient energy to become dissociated. It now becomes more probable that another HI molecule will strike the adsorbed one at just the correct orientation for reaction. Heterogeneous catalysts are indeed quite effective in increasing the rate of decomposition of HI. The activation energy of 44 kcal/mole for the non-catalyzed reaction is reduced to 25 kcal/mole on the surface of platinum and 14 kcal/mole on the surface of gold.

The reaction between H_2 and O_2 is highly exothermic, but a mixture of the two gases may be kept indefinitely without reacting appreciably. Yet when the two gases are brought together on the surface of finely divided platinum, they burst into flame. Apparently the vibration frequency is altered so much that the oxygen molecules actually dissociate into atoms with the necessary activation energy to react when struck by a hydrogen molecule.

Answers to Exercises and Problems

Exercise 12-1

Assume that you have 1 mole of HI gas in a 1-liter flask at 400°C .

- What is the concentration of HI, in moles per liter?
- What would the concentration be if the same amount of HI were put in a 500 ml flask?
- Predict whether the reaction will be faster in (a) or (b).

Answer

- 1 M
- 2 M

- A reaction dependent on HI concentration would be faster in case (b).

Exercise 12-2

Reactions between gases and solids are very important, particularly in many industrial processes. On the reasonable assumption that gas molecules must collide with the solid for reaction to occur, compare the rates of reaction in these three situations. The same mass of solid is considered in each instance.

Gas molecules collide with solid

- (a) made of cubes 1 cm on edge.
- (b) made of cubes 10^{-1} cm on edge.
- (c) made of cubes 10^{-3} cm on edge.

Answer

The rate of reaction would be fastest in case (c) because there is greatest area of solid surface and thus most collisions per unit time. Case (b) is next and case (a) least rapid. The relative areas are 1 : 10 : 1000.

Exercise 12-3

Imagine five people working together to wash dishes. The first two clear the table and hand the dishes to the third person. He washes them and hands them on. The last two persons dry and stack them. Which step is likely to be the rate-determining step? Discuss how the rate of the overall process would be affected if a sixth person joined the group (a) as a table clearer; (b) as a second dishwasher; (c) as a dish dryer.

Answer

The dishwashing step is probably rate determining. A sixth worker would then not change the overall rate if he joined the clearers or dryers. As a second dishwasher, he would increase the rate, probably doubling it.

A second dishwasher would possibly cause another step to become rate determining—probably drying. Emphasize that there is always a step that fixes the rate. Eliminating one bottleneck only brings the next most limiting one into play.

Problem 1

The rate of movement of an automobile can be expressed in the units miles per hour. In what units would you discuss the rate of:

- (a) movement of movie film through a projector;
- (b) rotation of a motor shaft;
- (c) gain of altitude;
- (d) consumption of milk by a family;
- (e) production of automobiles by an auto assembly plant.

Answer

Many answers could be given. Some of them are:

- (a) Frames/second; feet of film/second;
- (b) Revolutions/minute, rpm;

- (c) Feet/second;
- (d) Quarts/week;
- (e) Hundreds of automobiles/day.

Problem 2

Pick the member of each pair having the greater reaction rate. Assume similar conditions within each pair.

- (a) Iron rusting or copper tarnishing.
- (b) Wax burning or paper burning.
- (c) Evaporation of gasoline or evaporation of water.

Answer

- (a) Iron rusts faster than copper tarnishes. The reactions are assumed to take place in ordinary air.
- (b) Paper burns faster than wax.
- (c) Gasoline evaporates faster than water.

Problem 3

Explain (at the molecular level) why an increase in concentration of a reactant may cause an increase in rate of reaction.

Answer

As the concentration of reactant molecules rises, the number of collisions per second involving that reactant rises. If the rate of reaction is at all limited by such collisions, the rate rises.

Problem 4

The rate of a gaseous reaction may increase if the total pressure is increased. State three methods by which the pressure of a gaseous system might be increased.

Answer

- (1) Decrease the volume of the container.
- (2) Increase the temperature at constant volume.
- (3) Add more molecules.
- (4) Initiate a reaction that produces more molecules than are consumed.

Problem 5

Give two factors that would increase the rate of a reaction and explain why these do increase the rate.

Answer

- (1) Temperature. An increase in temperature increases the number of particles having sufficient energy to produce fruitful collisions. Another factor, but less important

than the above, is that the average kinetic energy will be increased. This will result in greater velocities and hence more collisions per unit time.

- (2) Concentration. An increase in concentration will give more particles per unit volume and hence more collisions per unit time.
- (3) Catalyst. A catalyst that increases a reaction rate does so by providing a new mechanism. If the activation energy of the limiting step of the new mechanism is lower than the activation energy of the limiting step of the uncatalyzed reaction, then the rate is increased very much.

Problem 6

Do you expect the equation



to represent the mechanism by which ethylene, C_2H_4 , burns? Why?

Answer

No. As written, the reaction involves a four-body collision. This is not likely to occur. The simultaneous breaking of C—C bonds, C—H bonds, and O—O bonds and the forming of C—O bonds and H—O bonds is regarded as unlikely.

Problem 7

A group of students is preparing a ten-page directory. The pages have been printed and are stacked in ten piles, page by page. The pages must be: (1) assembled in order, (2) straightened, and (3) stapled in sets. If three students work together, each performing a different operation, which might be the rate-controlling step? What would be the effect on the overall rate if the first step were changed by ten helpers joining the individual assembling the sheets? What if these ten helpers joined the student working on the second step? The third step?

Answer

Step 1 is the rate-controlling step, since at best it would require more time than the other two steps. An increase of 10 helpers on Step 1 would be reflected in a considerable increase in rate. In this particular example a considerable increase in rate for Step 1 might eventually cause one of the other steps (e.g. Step 3) to become the rate-controlling step.

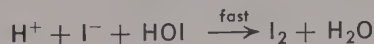
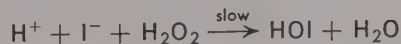
The same ten helpers on Step 2 or Step 3 would not increase the overall rate, since the slow Step 1 is the rate-controlling step.

Problem 8

Hydrogen peroxide reacts with iodide ion, according to this equation.



The mechanism often suggested for this reaction is



- (a) Satisfy yourself that addition of these two equations gives the overall equation.
- (b) How would you expect the rate to be affected if the I^- concentration is doubled?

Answer

- (a) Clearly addition does give the overall reaction.
- (b) In the rate-determining step I^- appears once. Therefore, doubling $[\text{I}^-]$ should double the rate.

Problem 9

Consider two gases *A* and *B* in a container at room temperature. What effect will the following changes have on the rate of the reaction between these gases?

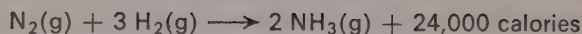
- (a) The pressure is doubled.
- (b) The number of molecules of gas *A* is doubled.
- (c) The temperature is decreased at constant volume.

Answer

- (a) Doubling the pressure increases the concentration of both reactants and consequently increases rate.
- (b) Doubling the number of molecules of *A* increases the concentration of *A* and hence may result in an increase in reaction rate.
- (c) Decreasing the temperature results in fewer molecules with sufficient energy to cause a reaction as well as fewer collisions per unit time, owing to a decrease in the kinetic energy of molecules. Both of these factors reduce the reaction rate. The first, however, is far more important than the latter.

Problem 10

In an important industrial process for producing ammonia (the Haber Process), the overall reaction is



A yield of approximately 98% can be obtained at 200°C and 1000 atmospheres of pressure. The process makes use of a catalyst which is usually finely divided, mixed iron oxides containing small amounts of potassium oxide, K_2O , and aluminum oxide, Al_2O_3 .

- Is this reaction exothermic or endothermic?
- Suggest a reason for the fact that this reaction is generally carried out at a temperature of 500°C and 350 atmospheres in spite of the fact that the yield under these circumstances is only about 30%.
- What is the ΔH for the reaction in kilocalories per mole of $\text{NH}_3(\text{g})$?
- How many grams of hydrogen must react to form 1.60 moles of ammonia?

Answer

- Exothermic.
- The higher temperature is used because the reaction rate is faster at 500°C. The 30% NH_3 can be easily separated (by liquefaction) and the unreacted N_2 and H_2 recycled. The lower pressure is used because of the cost of high-pressure equipment.
- $\Delta H = -12 \text{ kcal/mole of } \text{NH}_3(\text{g})$.
- Three moles H_2 give 2 moles NH_3 ;
 $\frac{3}{2}$ moles of H_2 give 1 mole NH_3 ;
 $(1.60)(\frac{3}{2})$ moles H_2 give 1.60 moles NH_3 ;
 $(1.60)(\frac{3}{2})$ moles $(2.02 \text{ g/mole}) = 4.85 \text{ g } \text{H}_2$;
4.85 g H_2 give 1.60 moles NH_3 .

Problem 11

Describe the life and death of an ordinary, empty water glass. Utilize the concept "threshold energy."

Answer

Ordinarily a glass experiences many bumps and knocks without being seriously damaged—not enough energy having been supplied to form a fracture in the network of atoms of which the material is made. A particularly sharp blow, however, can shatter the glass. A certain minimum amount of energy—the "threshold energy"—must be supplied before the glass will break.

Problem 12

Describe three situations at home or at school in which a minimum or threshold energy must be supplied before a "reaction" can take place.

Answer

opening a soft-drink bottle
opening a stuck window
starting a hard-set screw
pushing a stalled automobile
pressing the button on an aerosol can
flipping a light switch

Problem 13

Explain why food kept in a refrigerator does not spoil as rapidly as the same type of food left on the kitchen counter.

Answer

The growth of bacteria is the end result of many chemical reactions. These are slowed by the low temperature in a refrigerator. Also direct air oxidation of the food is slower at a low temperature.

Problem 14

An increase in temperature of 10°C rarely doubles the kinetic energy of particles and hence the number of collisions is not doubled. Yet, this temperature increase may be enough to double the rate of a slow reaction. How can this be explained?

Answer

A 10° rise in temperature is not much (about one-thirtieth of the absolute temperature at room conditions). Yet it has a large effect on many reaction rates. This results from the shape of the energy distribution curve (Textbook Figure 12-2). The extra kinetic energy resulting from the increased temperature increases the number of molecules having high energy. For many reactions, only a relatively few molecules have sufficient energy to be likely to react. The proportion of these is greatly increased by a temperature rise of even 10 C°.

Problem 15

In a collision of particles, what is the primary factor that determines whether a reaction will occur?

Answer

The primary factor is whether they collide with sufficient energy to exceed the activation energy and cause a reaction.

Problem 16

In Figure 12-11, why is kinetic energy decreasing as two HI go up the left side of the barrier and why is kinetic energy increasing as H_2 and I_2 go down the right side? Explain in terms of conservation of energy and also in terms of what is occurring to the various particles in relation to each other.

Answer

As the HI molecules approach each other more closely, the kinetic energy which they must possess in order to achieve this state is gradually changed to the potential energy of the activated complex. In achieving this state, the molecules had to overcome the mutually repulsive forces existing between them; hence the activated complex is highly unstable.

After its formation, the activated complex may

then either separate and return to the original reactants or rearrange and separate into the products. In either event, the relatively high potential energy possessed by the activated complex is changed into kinetic energy of the product molecules (or reactants if reaction is not completed).

Problem 17

Phosphorus, P_4 , exposed to air burns spontaneously to give P_4O_{10} ; the ΔH of this reaction is -712 kcal/mole P_4 .

- Draw an energy diagram for the net reaction, explaining the critical parts of the curve.
- How much heat is produced when 12.4 grams of phosphorus burn?

Answer:

See Figure 12-5.

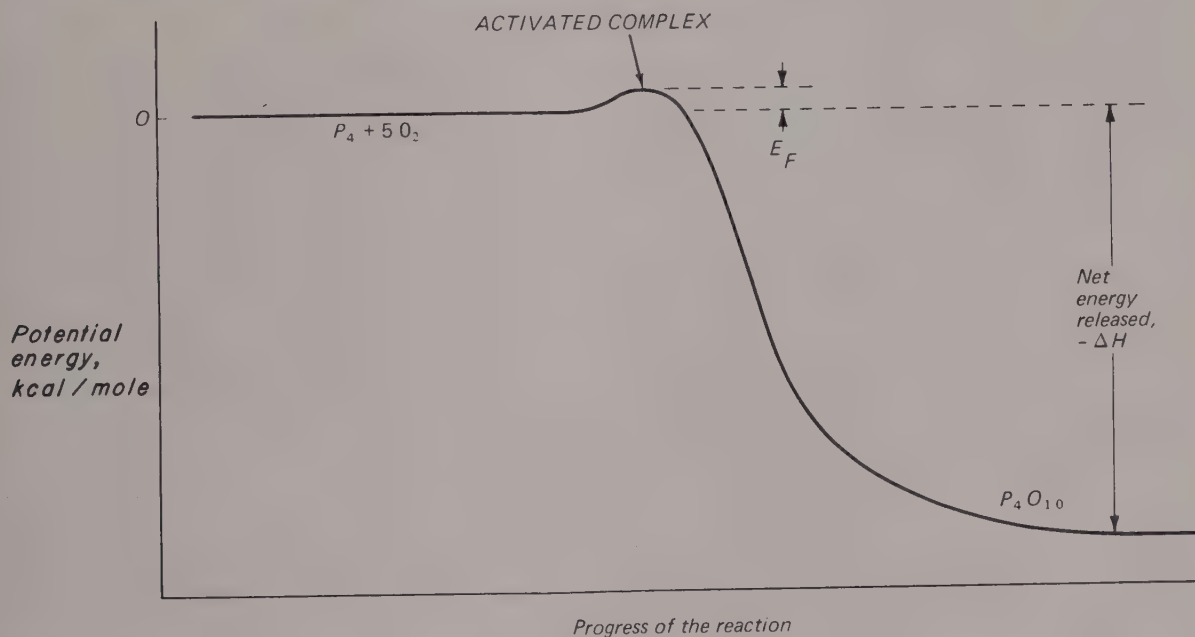
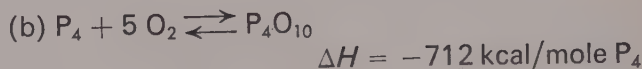


FIGURE 12-5

Potential energy diagram for the reaction $\text{P}_4 + 5 \text{O}_2 \rightleftharpoons \text{P}_4\text{O}_{10}$.

- Since the reaction is spontaneous, the curve must have at most a small energy barrier (small compared to kT). Activation energy is very low. The reaction is rapid and highly exothermic ($\Delta H = -712$ kcal/mole). The figure shows that the products have considerably less potential energy than the original reactants.



$$12.4 \text{ g P}_4 = \frac{12.4 \text{ g}}{124 \text{ g/mole}} = 0.100 \text{ mole}$$

$$(0.100 \text{ mole}) \left(712 \frac{\text{kcal}}{\text{mole}} \right) = 71.2 \text{ kcal heat}$$

produced by burning 12.4 grams P_4

Problem 18

Considering that so little energy is required to convert graphite to diamond (recall Problem 14, Chapter 11), how do you account for the great difficulty found in the industrial process for accomplishing this?

Answer

The activation energy must be very high. This would result in a very low rate of reaction.

You may wish to add these items to illustrate points discussed:

- (1) A high temperature is used. This increases the rate of both forward and reverse reactions; it also aids diffusion.
- (2) A high pressure is used. This favors the formation of the substance occupying the least volume. (This is an example of Le Chatelier's Principle, which the student will study in Chapter 13.) The density of diamond is 3.51 g/cc; of graphite, 2.25 g/cc.
- (3) A catalyst is used (a transition metal). This, according to our model, provides a route with a lower energy barrier.

Problem 19

Why does a burning match light a candle?

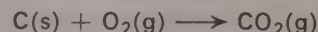
Answer

The activation energy of at least one reaction involved in the burning of a match head is

very low—so low, in fact, that the energy supplied to the match head by the abrasion during striking is sufficient to get that reaction going. The heat from it causes a series of reactions. Such is not true of the materials in the candle. These reactants have a greater "energy barrier." Rubbing the wick is not a practical way to supply enough activation energy. The energy from another source of heat, the match, is needed.

Problem 20

Draw an energy diagram for the reaction



- (a) when the C is in large chunks of coal.
- (b) Is the curve changed if very fine carbon powder is used?

Answer

- (a) Refer to Figure 12-6.
- (b) The curve is unchanged. The reaction will proceed faster, but the activation energy will remain the same, as will ΔH . The energy requirement for fruitful collisions is determined by the nature of the particles involved. It is true that the carbon powder will offer more opportunities for fruitful (as well as unfruitful) collisions, but the energy requirement for a fruitful collision remains unchanged.

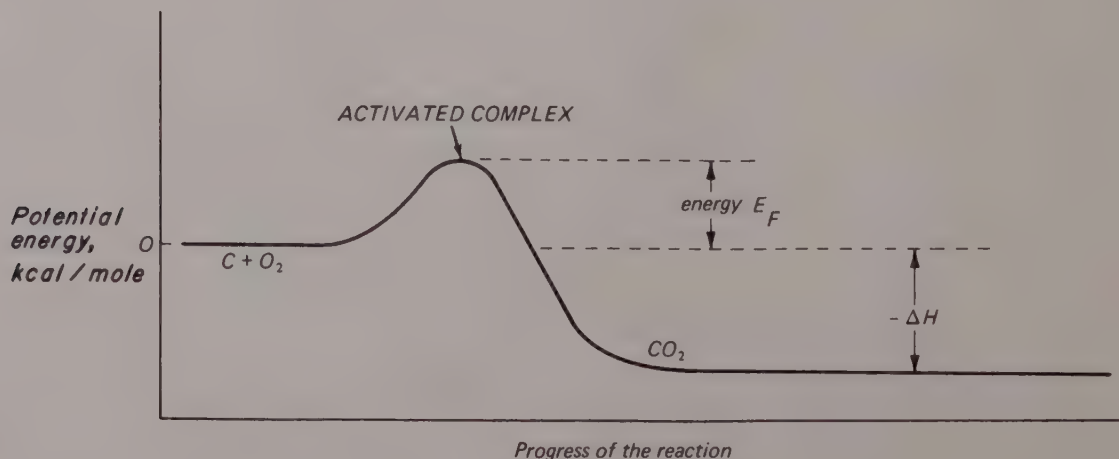


FIGURE 12-6

Potential energy diagram for the reaction $\text{C} + \text{O}_2 \rightleftharpoons \text{CO}_2$.

Problem 21

Sketch a potential energy diagram which might represent an endothermic reaction. Label parts of curve representing activated complex, activation energy, net energy absorbed, net energy absorbed.

Answer

See Figure 12-7.

Problem 22

Draw potential energy diagrams for two reactions that have the same ΔH but one reaction is fast and the other is slow.

Answer

See Figure 12-8.

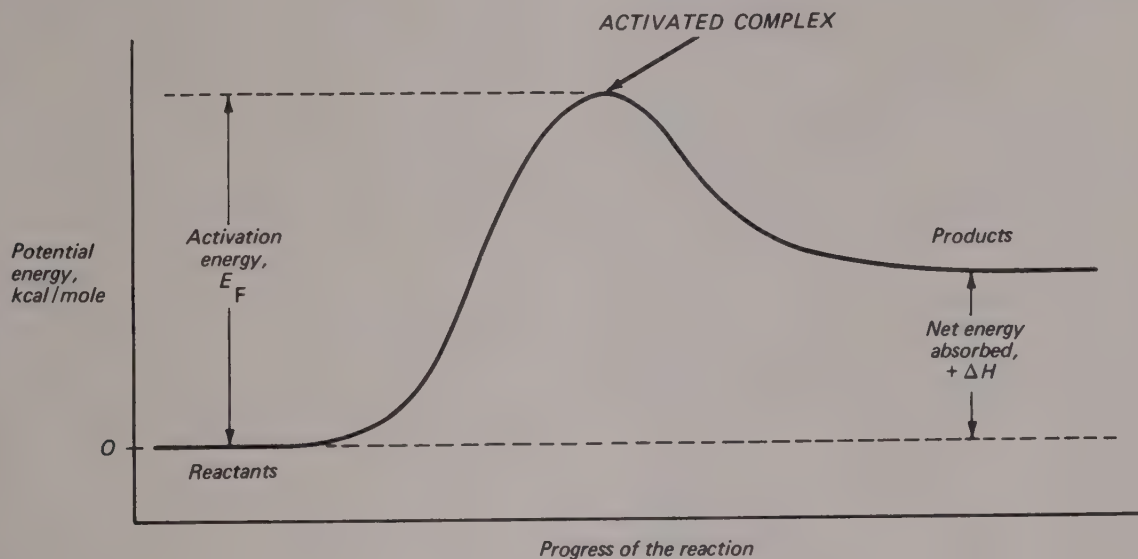


FIGURE 12-7

Potential energy diagram for an endothermic reaction.

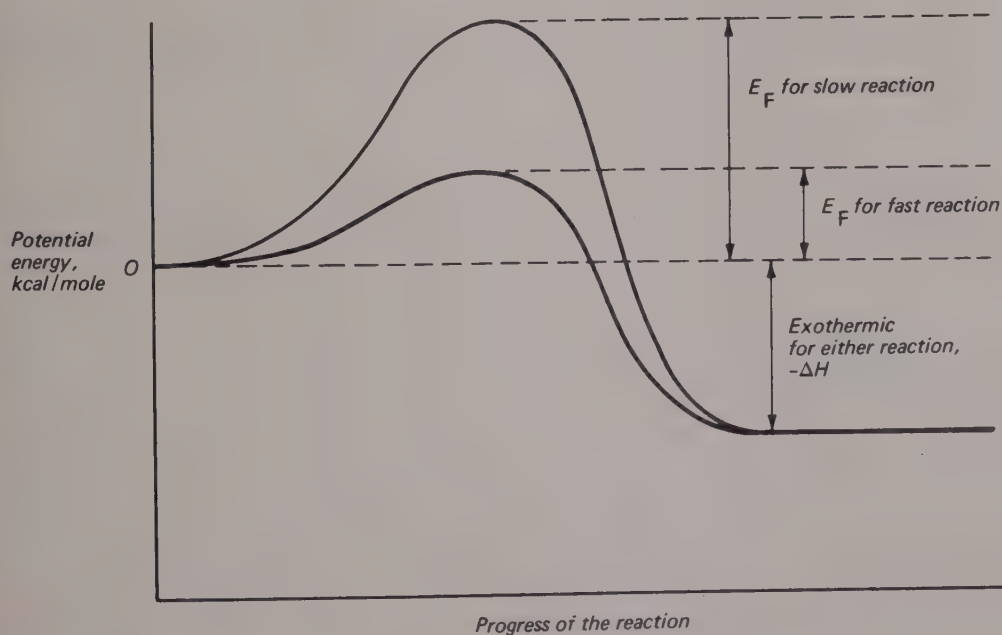


FIGURE 12-8

Potential energy diagram for two reactions having the same ΔH but different rates.

Problem 23

Why is it difficult to "hard-boil" an egg at the top of Pike's Peak? Is it also difficult to cook scrambled eggs there? Explain.

Answer

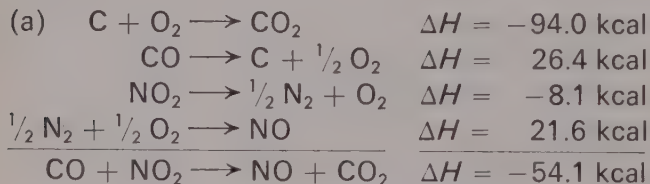
The egg being hard-boiled is heated by water that boils well below 100°C at this altitude. At this temperature not many molecules in the egg have enough energy to produce effective collisions. The cooking takes a long time. The scrambling process is not so hindered. The frying pan can easily be heated to essentially the same temperature as at sea level. Any water naturally present readily evaporates, and the egg cooks easily.

Problem 24

For the reaction $\text{CO} + \text{NO}_2 \longrightarrow \text{CO}_2 + \text{NO}$, the activation energy for the forward reaction is known to be $E_F = 32 \text{ kcal/mole}$.

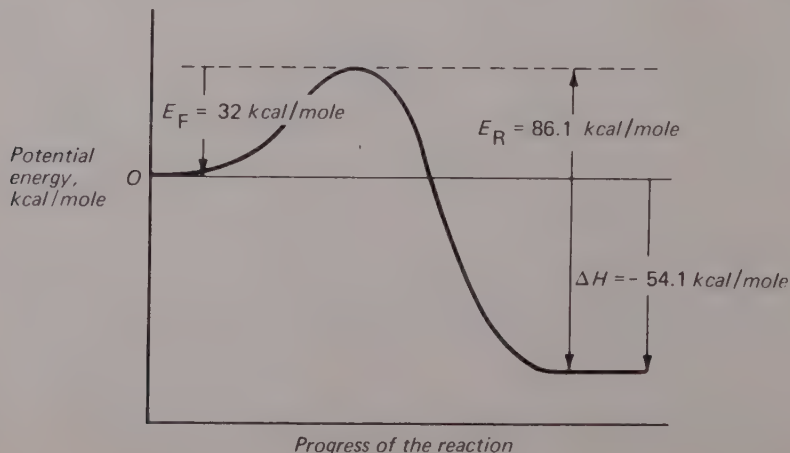
- Calculate ΔH for the reaction, using values from Table 11-2, p. 198.
- From E_F and ΔH , calculate E_R , the activation energy for the reverse reaction.
- Draw the potential energy diagram for this system, indicating E_F , E_R , and ΔH .

Answer



(b) $E_R = \Delta H + E_F = 54.1 + 32 = 86.1 \text{ kcal}$

(c)



Problem 25

Explain why a catalyst increases the rates of chemical reactions the same amount for both the forward and reverse reactions.

Answer

A catalyst provides a new reaction mechanism with a new level of potential energy in the activated complex. The difference between old and new level is subtracted from both E_R and E_F . The student answer will probably stop there. However, some student may ask why a given change in E_R and E_F should have the same effect when E_R does not equal E_F . The answer can come from the Arrhenius equation in the following way.

Forward Reaction

$$k_1 = Ae^{-E_F/RT}$$

Reverse Reaction

$$k_2 = Be^{-E_R/RT}$$

Modification by a catalyst lowers activation energy by $X \text{ kcal/mole}$.

$$k'_1 = Ae^{-(E_F-X)/RT}$$

$$k'_2 = Be^{-(E_R-X)/RT}$$

rewriting

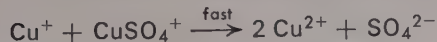
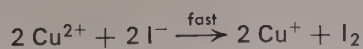
$$k'_1 = Ae^{-E_F/RT} e^{X/RT} = k_1 e^{X/RT}$$

$$k'_2 = Be^{-E_R/RT} e^{X/RT} = k_2 e^{X/RT}$$

Each new rate is the original rate multiplied by the same factor $e^{X/RT}$.

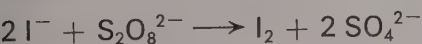
Problem 26

The reaction of $\text{S}_2\text{O}_8^{2-}$ with I^- is catalyzed by Cu^{2+} ions. A suggested mechanism involves these steps.



Add these equations to show that Cu^{2+} is not consumed in the overall reaction.

Answer



Problem 27

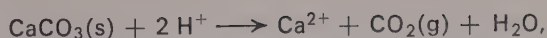
Explain why there is danger of explosion where a large amount of dry, powdered, combustible material is produced.

Answer

The tremendous increase in surface offers many more opportunities for collision between particles of combustible material and oxygen from the air. The rate of reaction goes up with the number of collisions. It is a type of concentration effect.

Problem 28

For the reaction of marble, $\text{CaCO}_3(\text{s})$, with acid,



compare the rate of reaction when $\text{CaCO}_3(\text{s})$ is in the form of large marble chips or in the form of a fine dust.

Answer

The large surface area of marble dust provides many more sites for reaction as H^+ ions collide with $\text{CaCO}_3(\text{s})$.

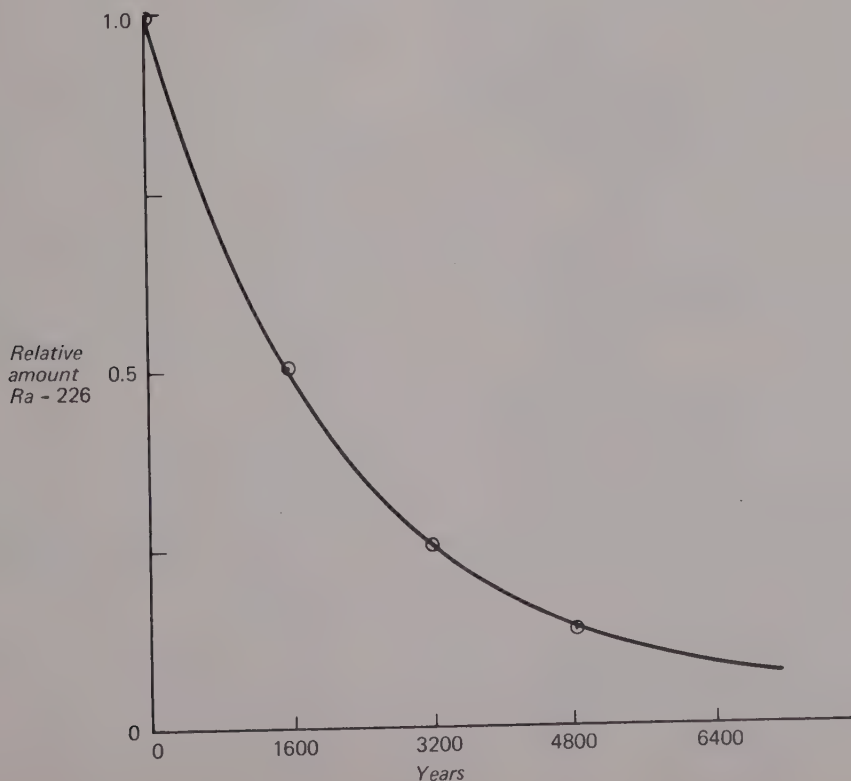
Problem 29

Ra-226 is a radioactive isotope of radium with a half-life of 1600 years. If you wait 1600 years, half of the radium you started with has undergone radioactive decay. If you wait another 1600 years you will have only one quarter of the radium you started with (one half of one half).

- Construct a graph of amount of Ra-226 as a function of time. Start with 1.0 gram of Ra-226 and show the amount after 1600, 3200, 4800, and 6400 years.
- Use your graph to estimate how much Ra-226 is present after one year, after ten years, and after 2400 years.

Answer

(a)



(b) Both one and 10 years are so short compared to 1600 years that we cannot read from the graph. The amounts left will be approximately $\frac{1599}{1600}$ and $\frac{1590}{1600}$ times the starting amount.

After 2400 years about 0.35 of the original amount will remain.

Problem 30

One gram of Ra-226 emits 3.7×10^{10} alpha particles per second. The nuclear reaction can be written



Calculate an approximate value for Avogadro's number. (In 1600 years, 0.5 gram of Ra-226 disappears. Compare the number of moles of Ra-226 with the total number of alpha particles given off in 1600 years.)

Answer

The decomposition of each Ra-226 nucleus produces one α particle.

$$\left(\frac{0.5 \text{ g Ra-226}}{226 \text{ g/mole}}\right) (N) = \left(\frac{3.7 \times 10^{10} \text{ particles}}{\text{sec}}\right) \times \left(365 \frac{\text{days}}{\text{yr}}\right) \left(86,400 \frac{\text{sec}}{\text{day}}\right) (1600 \text{ years})$$

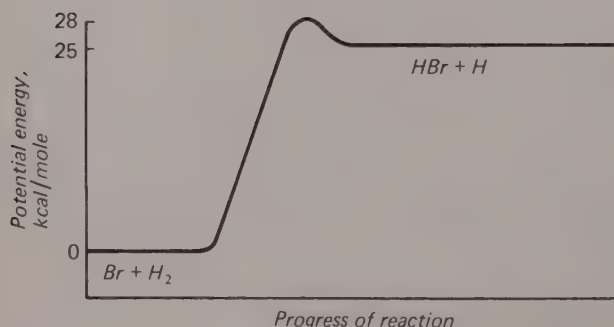
$$N = 3.7 \times 10^{10} \times 3.65 \times 10^2 \times 8.64 \times 10^5 \times 1.6 \times 10^4 \times \frac{226}{0.5} = 8.4 \times 10^{23} \text{ particles/mole}$$

This was one of the early ways to get values of Avogadro's number. See page 33.

Suggested Quiz Questions

The following questions are designed for an open book quiz. There are too many for a one-period test; make a selection to fit your class.

The figure below illustrates a potential energy diagram for the reaction represented by the equation



1. What is the heat of reaction, ΔH , in kcal/mole of HBr for the reaction $\text{Br} + \text{H}_2 \longrightarrow \text{HBr} + \text{H}$?

Answer: $\Delta H = 25 \text{ kcal/mole}$.

2. What is the energy of activation, E_F , for the reaction $\text{Br} + \text{H}_2 \longrightarrow \text{HBr} + \text{H}$?

Answer: $E_F = 28 \text{ kcal/mole}$.

3. What is the energy of activation, E_R , for the reaction $\text{H} + \text{HBr} \longrightarrow \text{H}_2 + \text{Br}$?

Answer: $E_R = 3 \text{ kcal/mole}$.

4. What would be the effect on the shape of the curve representing the path of the reaction if a catalyst were added?

Answer

The peak of the curve would be lowered approaching the 25 kcal/mole level.

5. Which portion of the curve represents the existence of an activated complex?

Answer

The peak at highest potential energy.

6. Is the reaction $\text{Br} + \text{H}_2 \longrightarrow \text{HBr} + \text{H}$ endothermic or exothermic?

Answer: Endothermic.

7. How does an increase in temperature affect the rate of a chemical reaction? Explain in terms of molecular kinetic energy.

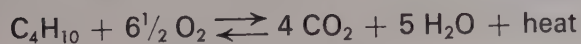
Answer

The rate is increased. A small increase in temperature greatly increases the number of molecules possessing greater than the minimum threshold kinetic energy.

8. Consider a flame which is produced as oxygen gas and butane, C_4H_{10} , burn to produce gaseous carbon dioxide and water. If butane is consumed at the rate of 2.24 liters/minute, (measured at STP), what is the rate of production of carbon dioxide in moles/minute?

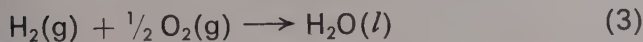
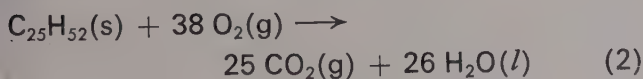
Answer

$$2.24 \text{ liters/minute} = 0.1 \text{ mole/minute}$$



For each mole of C_4H_{10} consumed, four moles of CO_2 are produced. The rate of production of CO_2 will be 0.4 mole/minute. This assumes a steady state condition.

For Questions 9 and 10 consider the following reactions as they occur at room temperature.



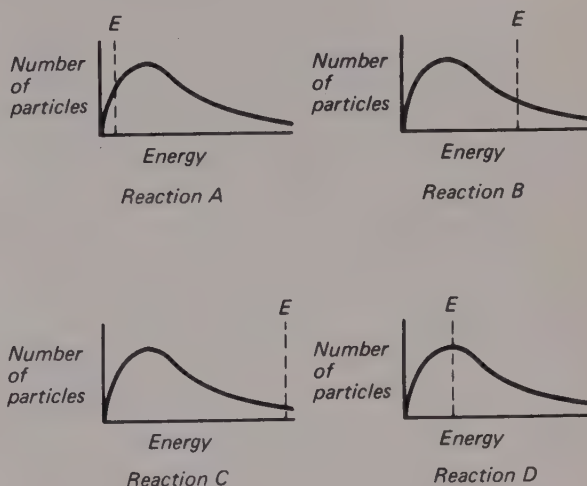
9. Which of the reactions, if any, may be extremely slow at room temperature?

Answer: (2) and (3).

10. Which of the reactions, if any, may be extremely fast at room temperature?

Answer: (1).

Consider the following identical kinetic energy distribution curves for four different reactions all at the same temperature. Only the threshold energy (E) is different.



11. Select the fastest and slowest reaction.

Answer

Fastest: reaction A.

Slowest: reaction C.

12. If a catalyst were added to a reacting system, what effect, if any, would this have on the kinetic energy distribution curve and on the threshold energy for the reaction?

Answer

Adding a catalyst to a reacting system does not change the kinetic energy distribution curve, but lowers the threshold energy requirement such that more molecular collisions are successful in producing reactions.

Equilibrium In Chemical Reactions



Intent and Approach

Two important questions capture the chemist's interest for all chemical reactions: How fast does the reaction proceed? To what extent does the reaction proceed in a given direction? In Chapter 12 we discussed the rate of chemical reactions. In this chapter our primary concern is the extent of a given reaction.

Emphasis should be placed on the dynamic nature of chemical equilibrium and on its relation to the rates of the opposing reactions. Le Chatelier's Principle is worth stressing as a tool for predicting the effect of various changes on the equilibrium of the system.

Here once again you have an excellent opportunity to introduce the student to one of the

frontier areas in chemistry. What are the factors which determine equilibrium? Why does one reaction favor the formation of products and a similar one the formation of reactants? The last section of this chapter proposes a model system for a chemical reaction which indicates that reactions will tend to proceed toward more stable molecular substances; i.e., those with lower energies. Yet many examples can be given to indicate that this is not always so, thus there must be another factor which determines or fixes the equilibrium state. This can be qualitatively described as the randomness implied by temperature.

Outline

Qualitative Aspects

Equilibrium is described as constancy of properties in a closed system (13-1).

The dynamic nature of chemical equilibrium is stressed. In chemical reactions, at equilibrium, microscopic processes continue, but in a balanced manner which yields no net change (13-2).

Altering the State of Equilibrium

The state of equilibrium, i.e., the relative concentrations of reactants and products, is not discernible from the balanced equation. This information must be obtained from other experimental data (13-3).

Equilibrium conditions for a given chemical system can be altered by changes in temperature, pressure, or concentration, but not by catalysts (13-4 to 13-6).

Le Chatelier's Principle (13-7) helps predict changes in equilibrium conditions.

Application of Equilibrium

The Haber process provides one example of an equilibrium reaction for which Le Chatelier's Principle aids in adjusting conditions (13-8).

Production of diamonds from graphite is another example (13-9).

Quantitative Aspects of Equilibrium

The equilibrium constant derived from experimental data (13-10, 13-11) relates the concentrations of reacting species in the equilibrium system.

Equilibrium Calculations

The solubility product, K_{sp} , is a particular type

of equilibrium constant (13-12). Its use for calculating solubility (13-13) and the possibility of precipitation (13-14) is discussed.

A brief introduction is given to two factors,

minimum energy and maximum randomness, that determine the equilibrium state (13-15).

A review (13-16) concludes the chapter.

New Concepts

1. Le Chatelier's Principle.
2. Law of chemical equilibrium—expression for equilibrium constant.
3. Factors that determine equilibrium conditions.
4. Equilibrium in a chemical reaction as a dynamic balance of microscopic changes.
5. Solubility product, K_{sp} .

SCHEDULE AND RELATED MATERIAL

Suggested Time : 12 days

Text Section	Topic and Other Work	Exercises	Problems		
			Easy	Medium	Hard
13-1	Qualitative Aspects of Equilibrium				
13-2	<i>Film:</i> Equilibrium				
	Recognizing Equilibrium		1, 2		
	Dynamic Nature of Equilibrium		3-5	6	
	Demo. 29. Chemical Equilibrium				
	Demo. 30. Depth and Color				
	Expt. 29. Chemical Equilibrium				
13-3	Altering the State of Equilibrium	1			7
13-4	Effect of Concentration Changes	2			8
13-5	Effect of Temperature Changes	3	9	10, 12	11
13-6	Effect of Pressure Changes		13	14, 15	
	Effect of Catalyst on Equilibrium				
13-7	Le Chatelier's Principle				
	Applications of Equilibrium				
	Principles				
	Expt. 30. Le Chatelier's Principle				
13-8	Synthesis of Ammonia				
13-9	Production of Diamonds				
	Quantitative Aspects of Equilibrium				
13-10	The Equilibrium Constant		17	18, 20	16, 19, 21
13-11	The Law of Chemical Equilibrium	4		23	22
	Equilibrium Calculations				
13-12	The Solubility Product	5-7		24	25, 26
13-13	Solubility of AgCl in H ₂ O	8		27	28
13-14	Will a Precipitate Form?	9		29, 30	31, 32
13-15	The Factors Which Determine Equilibrium		35	33, 36	34
	Demo. 31. Spontaneous Endothermic Reaction				

Development

QUALITATIVE ASPECTS OF EQUILIBRIUM

Introduction

The concept of chemical equilibrium is introduced by referring to the discussion in Chapter 12 concerning the rate of reaction between H_2 and I_2 and the rate of HI decomposition. When these rates are equal, the system attains constant properties and *seems* to stop reacting.

Chemical equilibrium is characterized by a lack of change in macroscopic processes resulting from the balance between the opposing processes still continuing at the molecular level.

13-1 Recognizing Equilibrium

An excellent beginning is made by the CHEM Study film "Equilibrium." This film uses a good analogy (many commonly thought of as steady state situations) and then uses the solubility of I_2 in alcohol-water as the principal chemical example.

Film, EQUILIBRIUM,

fits here. See p. 250 for summary.

Two other points of pedagogy must be mentioned here. The first is that when you describe attaining equilibrium and reach the point where there is "no visible change in processes," stress that this means there is *no observable* change. This will avoid confusion over the semantics involved in stating that there is no change, even though reactions in both directions are still going on. You can help clarify this by distinguishing between the *experimental facts* (lack of observable change) and the *interpretation* (reactions must be continuing). We do not have direct experimental proof of the second statement, since any experiment designed to detect changes will work only on a system which has not reached equilibrium! We believe reactions continue (unobserved) at equilibrium because this proposal is consistent with many kinds of data, the changes which occur in K , and our experi-

ence with the kinetic theory. The second point is that, in the Textbook and film examples, we have talked about only a few properties for each system—the color of $\text{NO}_2\text{--N}_2\text{O}_4$ gas, the color of I_2 solution, or the color and pressure of bromine gas. But at equilibrium *all properties become constant*.

The radioactive measurements in the film "Equilibrium" provide an example. The I_2 crystals and solution were at equilibrium (as shown by the color) when the radioactive iodine was added. It is clear that, at that instant, the balance was destroyed. The radioactive I_2 was not distributed in its equilibrium proportions. We then "watched" that distribution change by means of the Geiger counter. However, the point here is that we *observe change in a system not yet at equilibrium*. From this nonequilibrium behavior we make logical inferences about the solubility equilibrium of regular (nonradioactive) iodine.

As a second example, consider the often quoted (and demonstrated) case of a crystal hung in a temperature controlled saturated solution of the same material. The crystal will change shape, especially if it has broken edges. Yet the only reason change occurs is because equilibrium does *not* exist. Small crystals dissolve and large crystals grow *because small crystals dissolve faster*. The same is true of broken crystal faces; they dissolve faster than perfect faces. At equilibrium *no visible* changes occur.

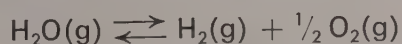
13-2 The Dynamic Nature of Equilibrium

The $\text{NO}_2\text{--N}_2\text{O}_4$ demonstration is used as a means of illustrating the dynamic nature of equilibrium processes. This experiment allows you to demonstrate (by means of easily observable color changes) the fact that in chemical reactions equilibrium involves continuing microscopic processes, but in a balance that results in no further macroscopic changes. The Textbook gives a good description, but the visual experience helps bring it to life.

Help the student realize that the equation for

the chemical reaction does not give any information about the actual concentrations of the products and reactants at equilibrium. These must be determined experimentally. The "state of equilibrium" for a particular system is described by the relative concentrations of products and reactants present at equilibrium.

Clarify this important point about the equilibrium state with the familiar reaction,



Until we are given additional information we have no idea how complete the decomposition of water is at equilibrium. All we know is that for each mole of water which decomposes we will obtain 1 mole of hydrogen and $\frac{1}{2}$ mole of oxygen.

Here is an example not given in the Textbook. It has been determined that in a closed vessel at 2273°K and a total pressure equal to one atmosphere at equilibrium, 0.6% of the water has dissociated. If we started with one mole of water, $0.6\% = 0.6 \times 1/100 = 0.006$ mole would decompose. There would be left $1 - 0.006 = 0.994$ mole of undecomposed water. There would be formed 0.006 mole of H_2 and 0.003 mole of oxygen. We can summarize:

	$\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$		
Initial moles	1	0	0
Moles present at equilibrium	0.994	0.006	0.003

In other words, if we start with water, not much of it has decomposed when the equilibrium state is attained at 2273°K.

Now what about approaching the equilibrium state by starting with hydrogen and oxygen? Let us start with 1 mole of hydrogen and $\frac{1}{2}$ mole of oxygen and allow the reaction to attain equilibrium at 2273°K and a total pressure equal to one atmosphere. At equilibrium we find present 0.994 mole of water, 0.006 mole of H_2 , and 0.003 mole of O_2 . This data can be summarized:

	$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$		
Initial moles	1	0.5	0
Moles present at equilibrium	0.006	0.003	0.994

If we start with hydrogen and oxygen, equilibrium is attained after most of the hydrogen and oxygen have united to form water. More important, though, the partial pressures at equilibrium are the same as those obtained beginning with pure H_2O . The equilibrium pressures are fixed by the temperature, the composition, and the total pressure; they do not depend upon the direction from which equilibrium is approached. The balanced equation does not indicate the concentrations (or partial pressures) at equilibrium. This attainment of the same "state of equilibrium" from all directions is an important experimental test of achieving equilibrium.

Note that in Figures 13-8 and 13-9 the same number of NO_2 units are maintained as the equilibrium state changes. Also the relative proportions of NO_2 and N_2O_4 are shown. However, the figures do not show the proper value of the equilibrium constant. The discrepancy arises because the correct value requires so many of one kind that the drawing would lose its effectiveness. The actual values of K are compared below with those calculated from the figures, " K ."

Temperature, °C	K actual	" K " from figure	" K " / 100
0	0.012	0.8	0.008
25	0.1	9	0.09
100	14	800	8

The " K " values are approximately 100 times larger than they should be. The same type of scaling is done in Figure 13-10. In Experiment 29, the student determines K to be about 300. The figures show 2.5 and 2.75. The two are essentially equal and nearly 1/100 the proper value.

ALTERING THE STATE OF EQUILIBRIUM

Changes in temperature, concentration, and pressure affect the conditions at equilibrium. Anything which affects the rate of one of the reactions involved in an equilibrium may affect the conditions that prevail at equilibrium.

Catalysts affect the rates of both the forward and the reverse reaction equally, and conse-

quently do not alter the equilibrium state. A section of the *Background Discussion* shows why this is so, p. 255.

You can ask for discussion of the consequences of various "disturbances" to the system. Let's describe these in terms of *increases* in the factors. Similar (but reverse) arguments will hold for decreases.

Demo. 29, CHEMICAL EQUILIBRIUM,

fits here. See p. 146 in the Laboratory Guide.

Demo. 30, DEPTH AND COLOR,

fits here. See p. 148 in the Laboratory Guide.

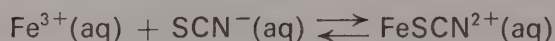
Expt. 29, CHEMICAL EQUILIBRIUM,

fits here. See p. 150 in the Laboratory Guide.

13-3 Effect of Concentration Changes

A concentration increase initially increases the number of one kind of molecule present in one ml. Since this molecule is involved in more collisions, the reaction using it becomes faster. This leads to a rise in the concentration of reactants for the reverse reaction, and so on. As a result of this rise, the concentrations of all species are changed. The same effect is achieved by increasing the partial pressure of one gaseous species.

The reaction



is to be used in Experiment 29 for the determination of an equilibrium constant. Introduce it now just to demonstrate the concentration effect. Show that adding more Fe^{3+} or SCN^{-} darkens the solution, indicating more FeSCN^{2+} .

13-4 Effect of Temperature Changes

A temperature rise will increase the average kinetic energy of all molecules. But the reactant molecules in the reaction that absorbs energy will begin to react somewhat faster. This will raise the

concentration of reactants for the reverse reaction and speed it up. A new equilibrium state will be reached in which products from the energy-absorbing reaction are increased.

13-5 Effect of Pressure Changes

In a practical sense, this discussion applies to gases only. The effect of pressure is quite like that of a concentration change. Higher pressures give more molecules per cubic centimeter. The reaction involving more gaseous species will be affected more because it is more dependent on concentration—there are more concentration terms in the rate equation. The reaction will produce more of the kind of molecules which act in the reverse way. This leads to a change in the reverse rate, and a new state of equilibrium is attained, in which more of the molecules having more atoms per molecule are favored. If there is no reaction leading to fewer total molecules, then no change in equilibrium results. All these effects are summed up by the statement: a change applied to a system at equilibrium causes reactions to occur so as to partially counterbalance the change.

The $\text{NO}_2\text{--N}_2\text{O}_4$ tube experiment can be referred to again at this point to demonstrate the effect of temperature. It can be quickly shown that different temperatures give different equilibrium states (color changes).

13-6 Effect of a Catalyst on Equilibrium

Catalysts have no effect on the relative concentrations at equilibrium. They do cause it to be attained more quickly. See p. 255 for some detailed discussion.

13-7 Le Chatelier's Principle: A Regularity

Before starting to explain Le Chatelier's Principle, remind the students of the dynamic equilibrium model. Point out that because of the differences in activation energy for the two reactions which are in balance, the number of molecules of reactants and of products will differ.

Use Table 13-1 (Textbook p. 236) to develop

the regularity. If the equilibrium state does shift, it will be in the direction expected from the heat and concentration terms but the shift may not be as large as expected. The "inverse" of Le Chatelier's Principle is seldom stated. You cannot change the equilibrium state except by applying some stress.

Expt. 30, APPLYING LE CHATELIER'S PRINCIPLE,

fits here. See p. 171 in the Laboratory Guide.

APPLICATIONS OF EQUILIBRIUM PRINCIPLES

13-8 The Synthesis of Ammonia by the Haber Process

This example affords the opportunity to predict the effect of various changes on the equilibrium conditions of a well-known commercial process. It serves as an excellent example of the importance of the rate of reaction. An increase in temperature results in the formation of less product, but unless the temperature is increased, no appreciable reaction will occur. At room temperature the rate is too slow for reaction to be economically useful. An increase in pressure favors increased yield of product. Here the cost of high pressure equipment results in a compromise. Removing the product (NH_3) and recycling the unreacted N_2 and H_2 result in further economy.

13-9 Production of Diamonds from Graphite

This second example provides some dramatic interest. Also it is more modern than the ammonia example although no more important. As yet it does not have nearly so great an importance as the fixation of nitrogen.

QUANTITATIVE ASPECTS OF EQUILIBRIUM

13-10 The Equilibrium Constant

Experiment 29 and the data for the $2 \text{HI}(\text{g}) = \text{I}_2(\text{g}) + \text{H}_2(\text{g})$ equilibrium given in this section

can be used by the student to find the relation between the concentrations of reactants and products at equilibrium. The advantage of this approach lies in the opportunity the better student has to discover this relation rather than having it imposed upon him.

13-11 The Law of Chemical Equilibrium

Use the relationship discovered in Experiment 29 and Section 13-10 to develop the law of chemical equilibrium. Given the reaction



we then have, at equilibrium,

$$\frac{[E]^e [F]^f}{[A]^a [B]^b} = K = \text{a constant}$$

Brackets are used in this expression to stand for concentration of substance, usually expressed in moles/liter.

In determining the value of K for a given reaction you omit the concentrations of any solid materials appearing in the reaction, since their concentration is fixed by their density and crystal structure and is constant for the reaction in question. In reactions involving water as one of the reactants or products (and carried out in an aqueous medium), the concentration of the water may be ignored in the equilibrium expression since usually only a tiny fraction of water is reacting. The concentration of water changes hardly at all. It can be considered a constant in the expression for the equilibrium constant. This approximation is most accurate for dilute solutions. Of course these "omissions" are conventions, and mean that the unvarying term is really still present, but as part of the constant itself.

Note that the student calculates this effect in Exercise 13-4. The effect can be larger than the exercise suggests. For instance in a 1 M solution of H_2SO_4 the water is present at 53.6 moles/liter. More concentrated solutions give greater differences from the 55.5 M value of pure water.

The student should have a firm feeling that a large K means products are favored—that is, the equilibrium mixture consists largely of products.

And of course the converse holds—a small K means reactants are favored.

Use a few, worked-out, simple examples to show that K is much greater than one when the products are in excess and vice versa. First, pick examples in which the balanced equation has no coefficients except one. Then gradually use the others. Choose the concentrations such that K is not near one but, instead, outside the range 0.01–100. For the more complicated reactions it is not easy to see what a value of K in this range means in terms of product concentration relative to reactant concentration; it depends upon the particular reaction.

Students should approach the calculations involving equilibrium constants by carefully noting what information is required and what information is given. The first step in most calculations involves setting up the expression for the equilibrium constant for the reaction being considered. At this point the student should tabulate what he knows about the experimental data connected with the reaction—i.e., the initial and final concentrations of reactants and products.

Near the end of this section, the student is reminded that water does dissociate into ions. K for the reaction is introduced. The equilibrium ion product for water, K_w , is quite important, primarily for the idea of balance that it expresses. Hydrogen and hydroxide ion concentrations are dependent upon each other. A simple analogy that may help is represented by a statement such as “Cut out a rectangular piece of paper containing 120 cm².” Many different shapes will result because different combinations of length and width will satisfy the requirements. Notice that the formula is similar to the ion product of water,

$$\text{Area} = (l)(w)$$

and that only one side may be chosen. The other is then set by the need to produce the constant area. The ion product, K_w , is found by experiment to be a constant. Many combinations of concentration values will yield this constant. When the molarity of one ion, $[\text{H}^+]$, is chosen, the other is fixed. It takes the value $K_w/[\text{H}^+]$.

A firm grasp of this interconnection will help in several later sections of the Textbook. The analogy is not, however, limited to K_w . It is true for all equilibria.

EQUILIBRIUM CALCULATIONS

13-12 The Solubility Product, K_{sp}

13-13 Calculation of the Solubility of Silver Chloride in Water

Present the solubility product constant as simply a special name for the equilibrium constant of one type of reaction—a slightly soluble material dissolving in an ionizing solvent. Most students flounder on the next step—finding the concentration of ions to substitute in the K_{sp} expression. Emphasize, therefore, that every problem, to be workable, must contain enough information to permit calculation of the moles/liter for each ion. Of course, in some problems (“What is the solubility of AgCl if the $K_{sp} = 1.7 \times 10^{-10}$?”) the whole point is to calculate the moles/liter from the solubility product constant. Practice is valuable here, hence you should assign several problems and work examples in class.

Although the point is a small one, we suggest that you avoid using the letter x as a symbol. It can be confused with the multiplication sign, especially in equilibrium problems, where exponential notation is often used, such as 1×10^{-3} . Use y , s , or the symbol for the ion concentration, e.g., $[\text{Cl}^-]$.

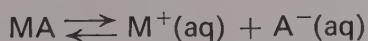
The units have been omitted from K_{sp} values. This is commonly done and should cause no confusion. They are always derived from ion concentrations in moles/liter.

Students often find it hard to develop the proper appreciation for solubility equilibria. You can use the experimental approach to prevent them from considering the problems in this chapter mere exercises in arithmetic. A series of test tube experiments will suffice. The following demonstration is an example.

Add two volumes of 1 M AgNO_3 to one volume of 1 M K_2CrO_4 , shake, and let settle. Decant

a small portion of the supernatant liquid, and add a few drops of 1 *M* KCl to it. The white precipitate shows that chromate ions did not precipitate silver ions completely from solution. It follows also that a smaller concentration of Ag^+ is required to precipitate AgCl than is required to precipitate Ag_2CrO_4 . The idea can be reinforced by adding a few drops of 1 *M* AgNO_3 to a solution which is 1 *M* with respect to both KCl and K_2CrO_4 ; AgCl will precipitate first. Another variation of the experiment is to precipitate Ag_2CrO_4 and then add KCl to the resulting mixture. Continued addition of KCl will cause red Ag_2CrO_4 to dissolve and white AgCl to precipitate. Experiments of this kind will convince the student that an equilibrium exists between a precipitate and its dissolved ions. See the *Supplementary Materials* of Chapter 6 (p. 103) for another example.

After you have established that an equilibrium exists between a precipitate and its dissolved ions, you will want to demonstrate the reciprocal relation between the concentrations of the ions in solution. The goal is to be sure that the student understands how a change in the concentration of one ion will affect the concentration of another ion. To illustrate this relation prepare a saturated solution of AgCl. Decant two portions of the clear liquid. Add a few drops of 1 *M* HCl to one, and a few drops of 1 *M* AgNO_3 to the other. The cloudiness produced in each portion shows that the solubility of AgCl can be decreased by adding either Ag^+ or Cl^- . It follows from the discussion above that for a reaction defined by the equation



and represented by the equilibrium constant expression

$$[\text{M}^+][\text{A}^-] = K_{\text{sp}}$$

a high concentration of one ion requires a small concentration of the other. That the product of the two concentrations should be a constant is no longer surprising.

Be careful not to add too much Cl^- . A complex will form and the AgCl will dissolve.

13-14 Will a Precipitate Form?

The student should also understand how to use the K_{sp} to decide whether a precipitate will form in a particular mixture. Keep the terms "solubility product" (equilibrium value of the concentration product) separate from "ion product" (just the product of ion concentrations as they would exist if nothing happened). The ion product comes straight from the stated problem, and the prediction follows from a comparison of the ion product with the K_{sp} .

13-15 The Factors Which Determine Equilibrium

The "golf ball" analogy described in this section is an attempt to give the student some insight into the factors which determine equilibrium. So far we have discussed those factors which can alter the conditions of a given equilibrium. We are now interested in what possible explanations can be advanced to account for the fact that one reaction will favor products whereas another will favor reactants.

The analogy as first used here implies that all exothermic reactions proceed spontaneously, which is in keeping with our experience for many reactions. It further implies, however, that an exothermic process would not reverse itself. This is not found to be so. Further, some endothermic or energy-absorbing processes occur spontaneously. Our first model does not offer an explanation for these phenomena.

It is clear that some other factor (entropy) in addition to minimum energy fixes the equilibrium state. Entropy is an expression of the randomness implied by temperature and is discussed in the background sections of this chapter and of Chapter 5. At any given time some of the product molecules in a chemical reaction may possess very high energies indeed, and may react to form the original substances.

You should stress this important fact. Even in a spontaneous, highly exothermic reaction, where most of the product molecules do indeed have relatively low potential energies compared to the reactant molecules, *some* of the product

molecules will have sufficiently high random thermal energies to cause the reverse reaction to occur. At higher temperatures the energy difference between reactants and products becomes less and less important because there is so much randomness caused by thermal motion. You may want to call particular attention to the brief discussion, at the end of this chapter, of some of the implications which can be drawn from the above concept. In particular, free energy is

quite important although it is not pursued in this course.

Demo. 31, SPONTANEOUS ENDOTHERMIC REACTION,

fits here. See p. 175 in the Laboratory Guide.

13-16 Review

Supplementary Material

Articles

S. Z. Levin and R. S. Wagner, "The nature of iron(III) thiocyanate in solution," *J. Chem. Education*, **30**, 445-450 (1953). This paper (useful for teachers) gives information about the nature of the compound in Expt. 29.

Films

For ordering information see the *List of Film Sources* at the back of the Teacher's Guide.

EQUILIBRIUM

A CHEM Study film

Running Time: 20 minutes

This film was produced in collaboration with Dr. G. C. Pimentel and fits quite closely with the Textbook. Several Textbook figures are directly related to it.

The film demonstrates through the use of radioactive tracers the constancy of macroscopic properties at equilibrium and the dynamic nature of the equilibrium state.

Four examples are used, the property in parentheses becoming constant at equilibrium.

1. Population of goldfish in a pair of goldfish bowls connected by a tunnel (population).
2. Gas pressure of bromine gas between two gas bulbs (gas color and pressure).
3. Solubility of I_2 in an alcohol-water mixture (solution color).
4. Reaction of I_2 with water:

$$3 I_2 + 3 H_2O = 5 I^-(aq) + IO_3^-(aq) + 6 H^+(aq)$$
(solution color).

Next the dynamic nature of equilibrium is demonstrated by allowing equilibrium to be attained and then adding radioactive material. Though the "constant" properties do not change, the radioactive material steadily distributes itself throughout the system. *The conceptual meaning of the tracer experiment* is first illustrated with marked fish. Then, in each example, the dynamic nature is shown.

Background Discussion

The chemist is concerned greatly with the extent of chemical reactions, for this knowledge permits him to predict whether a given reaction will be suitable for a specific purpose. Perhaps one of the most universal generalizations of chemistry is: all reactions tend to proceed to equilibrium. We say "tend to proceed" because, for most reactions to reach equilibrium, the necessary activation energy must first be applied. In Chapter 13 you will discuss how chemical equi-

librium is achieved kinetically; how equilibrium constants are measured and computed; how equilibrium concentrations can be altered to increase the formation of a desired product; and how equilibrium constant data are used to compute yields.

Up to now you have implied that the driving force of a chemical reaction is the energy released by the reactants in achieving a state of lower energy, and the golf ball analogy (Sec. 13-15)

supports this assumption. You know, however, that many reactions proceed spontaneously while absorbing energy. Apparently the direction of a chemical reaction is influenced by some factor other than the achievement of a lower energy state.

The following sections contain material on these topics:

Why Do Reactions Attain Equilibrium?

The Equilibrium Constant

The Relationship between the Equilibrium Constant and Free Energy

The Effect of Some Factors on Equilibrium Constants

The Variation of the Equilibrium Constant with Temperature

Two Contrasting Solubility Phenomena

Why Do Reactions Attain Equilibrium?

You may find a graphical representation of how a reaction achieves equilibrium a helpful aid in teaching the concept. An example of the form commonly employed is shown in Figure 13-1.

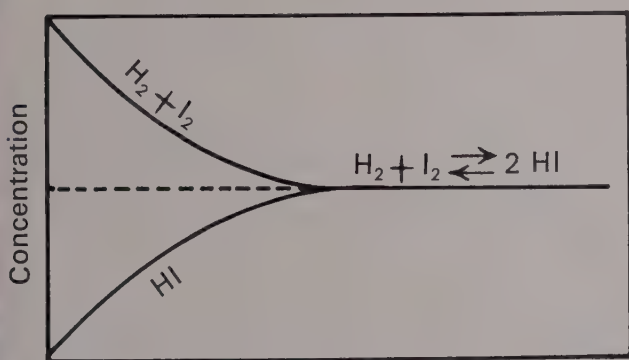


FIGURE 13-1

Concentration changes in a system approaching equilibrium.

You should remember, this curve represents the observations but *not* the reaction mechanism. Observe that, at the time of mixing, the rate of formation of HI is quite large and that the rate of consumption of H_2 and I_2 is also large. It follows that the concentrations of H_2 and I_2 will decrease with time, whereas the concentration of HI will increase. Since rate of reaction de-

pends upon the concentration of the reactants, we expect the rate of formation of HI to decrease with time. Furthermore, its rate of decomposition should increase. Since the two rates are in opposition, they must eventually become equal. The state in which the rate of the reverse reaction becomes equal to the rate of the forward reaction is defined as chemical equilibrium.

The student may experience difficulty understanding why products should re-form reactants. He may reason that if products are going to re-form reactants, why do the reactants combine in the first place. This is where you should suggest that the tendency to reach minimum energy is not the only factor that induces chemical reaction.

Normally one expects a reaction to proceed in the direction in which energy is released. If an isolated H_2 molecule reacted with an isolated I_2 molecule to form two isolated HI molecules—that is, two which never collided—the reaction might be completed in the direction of the formation of HI. In an actual reaction, however, moles of H_2 react with moles of I_2 to form moles of HI. This means that billions of billions of both reactant and product molecules are involved. Remember that, although the average energy state of H_2 and I_2 molecules is higher than the average energy state of two HI molecules, reaction does not occur between molecules in the average energy state but between those in an activated state.

The Equilibrium Constant

The previous discussion should make the qualitative nature of chemical equilibrium reasonably clear. Now you wish to go further and examine the quantitative aspects. Reaction rate equations are convenient vehicles for deriving equilibrium constant expressions. Observe that K is a ratio of the rate constant for the forward reaction divided by the rate constant for the reverse reaction. It follows that K must be related to the basic tendency of the reactants to react. Its value tells the extent to which the reaction has proceeded at equilibrium. The equilibrium constant may be evaluated from a knowledge of the con-

centrations of the various chemical species at equilibrium.

The utility of the equilibrium constant expression lies in our ability to use it to predict the conditions that will produce a desired product and to calculate what yield can be expected.

One of the great advantages of the equilibrium constant expression is its universality. It applies to all chemical reactions. The Textbook gave examples of some reactions to which the equilibrium constant expression applies in Tables 13-4 and 13-5. Other examples are listed here in Table 13-1. Observe that the concentrations of

the species which are not changed appreciably during reaction are not included in the equilibrium constant expression. The constant concentrations are put "in with" K .

It is because chemical equilibrium is involved in the whole of chemistry that we devote so much time to it. The details of how to apply quantitatively the equilibria listed below are given in the references at the end of the chapter.

The Relationship between the Equilibrium Constant and Free Energy

The equilibrium constant is a convenient quan-

Table 13-1
Examples of the Application of the Equilibrium Constant

Vapor Pressure



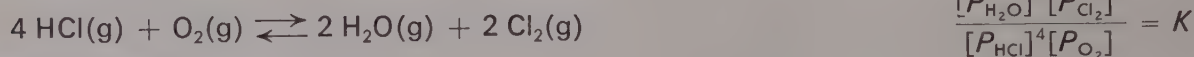
Solubility



Extraction



Gas Reaction



Gas Dissociation



Solid Dissociation



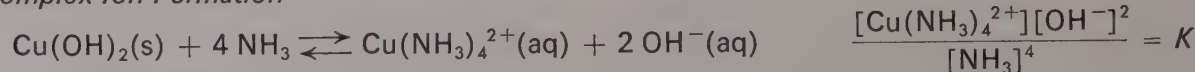
Acid Reaction



Base Reaction



Complex Ion Formation



Oxidation-Reduction



titative statement of the state of equilibrium. The equilibrium constant expression can be used to compute the expected extent of reaction from chemicals mixed at any initial set of concentration conditions. Because of its great importance, we should like to know the equilibrium constant for as many reactions as possible. From our discussion up to now, the only method of obtaining it consists in carrying out the reaction and measuring the concentrations of the reactants and products at equilibrium. Such a procedure limits the availability of equilibrium constant data, for the equilibrium state of many reactions is difficult to obtain; moreover, it would be most convenient to be able to obtain the equilibrium constant without having to carry out the reaction.

We learned in Chapter 8 that the tendency of a reaction to form products is connected with the change in energy which the reactants undergo. Since energy changes often can be conveniently and precisely determined, a knowledge of the exact relation between equilibrium constant and energy change would aid us materially in obtaining equilibrium constants. The remaining discussion in this section is designed to establish this relation qualitatively.

In Chapters 11 and 12 we found that most reactions which proceeded readily, once the necessary activation energy was applied, were exothermic. It appears from this observation that the energy released in an exothermic reaction might be used as a measure of the tendency of the reaction to proceed. We know, however, that some reactions which liberate more heat proceed to a smaller extent than do other reactions that liberate less heat. To confuse the picture even more, some endothermic reactions proceed spontaneously. Examples given in Chapter 13 of the Textbook were the evaporation of water and the dissolution of NH_4Cl in water. The real driving force of a chemical reaction appears to include the achievement of the state of greatest random distribution of energy; that is, the state of least restraint. The Textbook has referred to this kind of energy distribution as the randomness implied by the temperature. The property which

measures the degree of randomness of energy distribution is called the *entropy*.

Thus, the reaction tendency is expressed as the competition, or balance, between two tendencies.

$$\left(\begin{array}{c} \text{Reaction} \\ \text{tendency} \end{array} \right) = \left(\begin{array}{c} \text{Tendency} \\ \text{toward} \\ \text{minimum} \\ \text{energy} \end{array} \right) - \left(\begin{array}{c} \text{Tendency} \\ \text{toward} \\ \text{maximum} \\ \text{randomness} \end{array} \right)$$

You have already established that ΔH is a measure of the tendency toward minimum energy. The golf ball analogy hints at the random tendency, which is quantitatively expressed as $T\Delta S$ (temperature $\times$ change of entropy). The temperature factor indicates that a greater state of randomness can be achieved as the equilibrium system is heated.

$$\left(\begin{array}{c} \text{Reaction} \\ \text{tendency} \end{array} \right) = \Delta H - T\Delta S$$

Net reaction stops when equilibrium is reached—our operational definition of equilibrium. This must mean that the reaction tendency, called free energy (ΔG), is zero. Thus at equilibrium

$$\Delta G = 0 = \Delta H - T\Delta S$$

Incidentally, ΔG , when different from zero, is equal to the maximum useful work that can be derived from the system as it changes toward equilibrium. Since the work must come *out of the system*, useful work is written $+w$. The system *loses* the work, and so ΔG must decrease in a process which can do useful work. Such a process is called spontaneous.

An important example occurs when only electrical work is done. Then $\Delta G = -nEF$, an equation which we will discuss in the guide for Chapter 15. This equation is the basis for an important way of measuring ΔG , and illustrates why chemists are concerned with E .

A chemical reaction may be considered to be a process which, together with its surroundings, constitutes a system. In accordance with the analogy made above, ΔG can be used as a measure of the "driving force" of a chemical reaction.

Free energy and work are connected:

- (a) $w = 0$, no work can be obtained, $\Delta G = 0$, the reaction must be at equilibrium;
- (b) w is positive, the system can do work, ΔG is negative, the reaction can proceed spontaneously;
- (c) w is negative, no work can be obtained, ΔG is positive, energy must be supplied to induce the reaction.

(The idea that a chemical reaction can do work is well illustrated by burning coal to drive a train.) The ability to use ΔG to predict whether a chemical reaction can proceed makes this one of the most powerful properties available to the chemist. In Chapter 11 you might have been tempted to teach, or at least to imply, that ΔH was a reasonable indication of whether a reaction could proceed spontaneously. You see now that ΔG is the proper guide to spontaneity. It is perhaps too complex to present to the high school student. It is true that ΔG and ΔH are frequently close together (whenever $T\Delta S$ is small). Under these conditions ΔH may be taken as a good approximation of the tendency of a reaction to proceed. From the equation, we see also that when $T\Delta S$ is much larger than ΔH , ΔG can be negative even though ΔH is positive; in such cases endothermic reactions will proceed spontaneously. The science which relates energy of reactions and their tendency to proceed is called *thermodynamics*.

We have found that free energy is a measure of the driving force of a chemical reaction. We know that the tendency of a reaction to proceed depends upon the nature of the reactants and their concentrations.

$$\Delta G = f(N, C) \quad (1)$$

where N refers to the nature of the reactants and C to their concentrations. The exact equation derived in thermodynamics and applied to the general reaction $aA + bB = eE + fF$ is

$$\Delta G = \Delta G^\circ + 2.3 RT \log \frac{[E]^e [F]^f}{[A]^a [B]^b} \quad (2)$$

Here ΔG° , called the change in standard free energy, is a constant which depends upon the nature of the reactants. The brackets are the symbol for concentration. We have seen above that the condition $\Delta G = 0$ defines a state of equilibrium; thus under equilibrium conditions equation (2) becomes

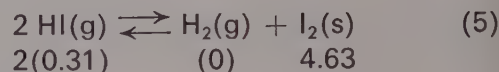
$$0 = \Delta G^\circ + 2.3 RT \log \left(\frac{[E]^e [F]^f}{[A]^a [B]^b} \right)_{\text{eq.}} \quad (3)$$

In the Textbook $\left(\frac{[E]^e [F]^f}{[A]^a [B]^b} \right)_{\text{eq.}}$ is equal to the equilibrium constant K , thus equation (2) can be written

$$\Delta G^\circ = -2.3 RT \log K \quad (4)$$

The discussion in this section was designed to show qualitatively how equation (4) was obtained. One of the main uses of this equation is for computing equilibrium constants.

The standard free energy of reaction is usually computed from standard free energies of formation which have been measured and tabulated in books on physical chemistry. *The Handbook of Chemistry and Physics* contains comprehensive tables. The method may be illustrated by computing the equilibrium constant for the dissociation of HI at 25°C.



The free energies of formation are written beneath the reactants. The standard free energy of reaction is

$$\begin{aligned} \Delta G^\circ &= 0 + 4.63 - 2(0.31) \\ &= 4.01 \text{ kcal/mole} \end{aligned}$$

Substituting this value of ΔG° , along with the appropriate values of the other terms, yields

$$\begin{aligned} 4010 \text{ cal mole}^{-1} \\ = -2.30 \times 1.99 \text{ cal mole}^{-1} \text{ deg}^{-1} \times 298^\circ \log K \end{aligned}$$

This equation is satisfied by $K = 1.3 \times 10^{-3}$. Observe that K , the equilibrium constant for the dissociation of HI, is much smaller at room temperature than the value 1.84×10^{-2} at 700°K , given in Table 13-3 of the Textbook, p. 239.

The Effect of Some Factors on Equilibrium Constants

On p. 228 the simple Arrhenius equation is given as $k = Ae^{-\Delta H^\ddagger/RT}$. The term $\Delta H^\ddagger$ is activation energy which was simplified to E in the Textbook. Now you can understand that a more correct version is

$$k = Ae^{-\Delta G^\ddagger/RT} = Ae^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R}$$

For greater readability we write $\exp(-\Delta G^\ddagger/RT)$ instead of $e^{-\Delta G^\ddagger/RT}$, giving

$$k = A \exp(-\Delta G^\ddagger/RT) \\ = A \exp(-\Delta H^\ddagger/RT) \exp(\Delta S^\ddagger/R)$$

We can use this equation to show the effect of temperature and catalyst on equilibrium constant. If we equate the reaction rates "to the right" and "to the left" then

$$K = \frac{k_{\text{right}}}{k_{\text{left}}} = \frac{k_r}{k_l}$$

Let us examine the effect of a catalyst first. We have omitted the symbol $\ddagger$ from each Δ term, although an activated complex is intended.

$$k_r = \exp(-\Delta G_r/RT) \\ = \exp(-\Delta H_r/RT) \exp(\Delta S_r/R)$$

$$k_l = \exp(-\Delta G_l/RT) \\ = \exp(-\Delta H_l/RT) \exp(\Delta S_l/R)$$

$$K = \frac{k_r}{k_l} = \frac{\exp(-\Delta H_r/RT) \exp(\Delta S_r/R)}{\exp(-\Delta H_l/RT) \exp(\Delta S_l/R)}$$

When a catalyst is added, *both* ΔH_r and ΔH_l are lowered by an amount ΔH_c , where the subscript c shows that a catalyst is present. The change

in entropy, ΔS , is affected in a similar way because a new activated complex, with a different randomness, is involved. Then we write

$$k_r = \exp\left(\frac{-\Delta H_r}{RT}\right) \exp\left(\frac{\Delta H_c}{RT}\right) \exp\left(\frac{\Delta S_r}{R}\right) \exp\left(\frac{-\Delta S_c}{R}\right)$$

$$k_l = \exp\left(\frac{-\Delta H_l}{RT}\right) \exp\left(\frac{\Delta H_c}{RT}\right) \exp\left(\frac{\Delta S_l}{R}\right) \exp\left(\frac{-\Delta S_c}{R}\right)$$

$$K_c = \frac{k_r}{k_l} = K \frac{\exp(\Delta H_c/RT) \exp(-\Delta S_c/R)}{\exp(\Delta H_c/RT) \exp(-\Delta S_c/R)} = K$$

The changed factors cancel out, and K is not altered.

For a change in temperature, start by writing

$$\Delta H_r = \Delta H_l + \Delta H$$

We can ignore the ΔS term in

$$K_T = \frac{k_r}{k_l} = \frac{\exp(-\Delta H_r/RT)}{\exp(-\Delta H_l/RT)} \\ = \frac{\exp(-\Delta H_l/RT) \exp(-\Delta H/RT)}{\exp(-\Delta H_l/RT)} \\ = \exp(-\Delta H/RT)$$

Thus when we change T to $(T + \Delta T)$ we obtain

$$K_{(T+\Delta T)} = \exp[-\Delta H/R(T + \Delta T)]$$

This is *not* equal to K_T .

The Variation of the Equilibrium Constant with Temperature

In the preceding section, we computed, using thermochemical data, the equilibrium constant for the dissociation of HI at room temperature as 1.5×10^{-6} . In the Textbook, using experimental equilibrium concentrations measured at 700°K , we computed the equilibrium constant for the same reaction to be 1.84×10^{-2} . Can we compare the two computations? Clearly, we are asking whether equilibrium constants at one temperature can be computed from those measured at another temperature. We seek to know how equilibrium constants vary with temperature. One approach to this question is to differentiate equation (4) with respect to temperature.

This yields

$$\begin{aligned}\frac{d\Delta G^\circ}{dT} &= -2.3R \left(T \frac{d \log K}{dT} + \log K \right) \\ \frac{d\Delta G^\circ}{dT} &= -2.3RT \frac{d \log K}{dT} - 2.3R \log K \quad (6)\end{aligned}$$

Multiplying by T gives

$$T \frac{d\Delta G^\circ}{dT} = -2.3RT^2 \frac{d \log K}{dT} - 2.3RT \log K \quad (7)$$

Combining this expression with equation (4) gives

$$T \frac{d\Delta G^\circ}{dT} = -2.3RT^2 \frac{d \log K}{dT} + \Delta G^\circ \quad (8)$$

From thermodynamic theory,

$$T \frac{d\Delta G^\circ}{dT} = \Delta G^\circ - \Delta H^\circ,$$

thus

$$\Delta G^\circ - \Delta H^\circ = -2.3RT^2 \frac{d \log K}{dT} + \Delta G^\circ$$

or

$$\frac{d \log K}{dT} = \frac{\Delta H^\circ}{2.3RT^2} \quad (9)$$

Equation (9) defines the variation of the equilibrium constant with temperature. It is called van't Hoff's equation. Observe that if ΔH is positive (that is, if the reaction is endothermic), then the equilibrium constant will be greater at the higher temperature. In contrast, if ΔH is negative (that is, if the reaction is exothermic), then the equilibrium constant will be smaller at the higher temperature.

You can use equation (9) to test the predictions regarding the variation of the equilibrium constant with temperature which you studied in the Textbook in relation to Le Chatelier's Principle.

Integrating equation (9) between two temperatures, with the assumption that ΔH° is constant, gives

$$\log (K_2/K_1) = \frac{\Delta H^\circ}{2.3R} \left(\frac{T_2 - T_1}{T_2 T_1} \right) \quad (10)$$

Equation (10) can be used to compute K at one temperature from a knowledge of ΔH° and K at

another temperature. Unfortunately ΔH° is not constant, as has been assumed, but may vary with temperature. It does remain sufficiently constant, however, over small temperature intervals, 50–100°, to permit the use of equation (10). A more complicated equation in which ΔH is expressed as a function of temperature must be used in computations involving two widely separated temperatures. More about this must be sought in advanced texts.

Two Contrasting Solubility Phenomena

Solids dissolve more as temperature goes up;
Gases dissolve less as temperature goes up.

An analysis can be conveniently carried out by looking at the effect of randomness (ΔS), energy (ΔH), and temperature for each case.

SOLID IN LIQUID

We consider a solid first and take I_2 dissolving in CCl_4 as the example.

The Effect of Randomness

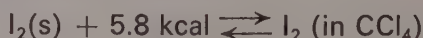
The dissolving process destroys the regular crystal lattice of iodine and forms the disordered solution. The dissolving process *increases* randomness. The tendency toward maximum randomness tends to cause solids to dissolve.

The Effect of Energy

Experiment shows that heat is absorbed as iodine dissolves. The regular, ideally packed iodine crystal gives an iodine molecule a lower potential energy than does the random and loosely packed solvent environment. We see that the second factor, tendency toward minimum energy, favors precipitation and growth of the crystal.

Now we see the opposing factors at equilibrium. To increase randomness, solid tends to dissolve. To lower energy, solid tends to precipitate. Equilibrium is reached when the concentration is such that these two tendencies are equal.

How much the energy factor favors the crystal depends upon the change in heat content as a mole of solid dissolves. This change is called the heat of solution. The heat of solution of iodine in CCl_4 has been measured.



The Effect of Temperature

Raising the temperature always tends to favor the more random state. For these solvents, this means that more solid will dissolve, since the liquid solution is more random than the solid. The solubility of iodine *increases* as temperature is raised, both in alcohol and in carbon tetrachloride.

GAS IN LIQUID

Gases, too, dissolve in liquids. Let us apply our understanding of equilibrium to this type of system.

The Effect of Randomness

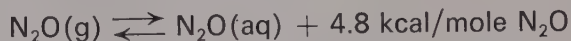
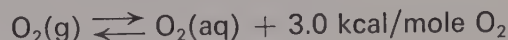
The gaseous state is more random than the liquid state since the molecules move freely through a much larger space as a gas. Hence randomness *decreases* as a gas dissolves in a liquid. In this case, unlike solids, the tendency toward maximum randomness favors the gas phase and opposes the dissolving process.

The Effect of Energy

In a gas the molecules are far apart and they interact very weakly. As a gas molecule enters the liquid, it comes close to the solvent molecules and they attract each other, lowering the potential energy. Again we find a contrast to the behavior of solids. When a gas dissolves in a liquid, *heat is evolved*. The tendency toward minimum energy favors the dissolving process.

Thus we see that the equilibrium solubility of a gas again involves a balance between randomness and energy as it does for a solid, but the effects are opposite. For a gas, the tendency toward maximum randomness favors the gas phase, opposing dissolving. The tendency toward minimum energy favors the liquid state, hence favors dissolving.

As an example, consider the solubilities of the two gases, oxygen, O_2 , and nitrous oxide, N_2O , in water. The heats of solution have been measured and are as follows:



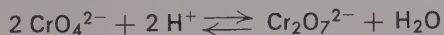
Assuming the randomness factor is about the same, the gas with the larger heat effect (favoring dissolving) should have the higher solubility. The measured solubilities at one atmosphere pressure and 20°C of oxygen and nitrous oxide in water are, respectively, O_2 , 1.4×10^{-3} mole/liter and N_2O , 27×10^{-3} mole/liter, consistent with our prediction.

The Effect of Temperature

Raising the temperature always tends to favor the more random state. This means that less gas will dissolve, since the gas is more random than the liquid. The solubility of a gas *decreases* as temperature is raised.

Answers to Exercises and Problems**Exercise 13-1**

Sodium chromate, Na_2CrO_4 , dissolves in water to give a yellow solution. Sodium dichromate, $Na_2Cr_2O_7$, dissolves in water to give an orange solution. In either reaction, the equilibrium equation is



- What would happen if you added hydrochloric acid to a solution of sodium chromate?
- What would happen if you added $Cr_2O_7^{2-}$ to the solution in part a?

Answer

- More $Cr_2O_7^{2-}$ would form; the solution would become more orange.
- Some $Cr_2O_7^{2-}$ would be converted to CrO_4^{2-} and H^+ ; the solution would be less orange than the added $Cr_2O_7^{2-}$ would have produced if no change occurred.

Exercise 13-2

How would the addition of more energy affect the amount of NH_3 at equilibrium in this reaction?

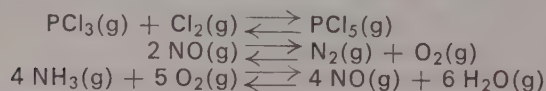


Answer

Added heat would decrease the amount of NH_3 .

Exercise 13-3

What happens in these gas phase equilibria if the volume of each system is increased by a factor of two?



Answer

$\text{PCl}_3 + \text{Cl}_2$ formation favored.

There would be no effect.

$\text{NO} + \text{H}_2\text{O}$ formation favored.

Exercise 13-4

- Water has a density of one gram per milliliter. Calculate the concentration of water in moles per liter in pure water.
- Now calculate the concentration of water in 0.10 *M* aqueous solution of acetic acid, CH_3COOH , assuming each molecule of CH_3COOH occupies the same volume as one molecule of H_2O .

Answer

- 1 liter = 1000 g of H_2O
1 mole = 18 g of H_2O

Thus, for pure H_2O ,

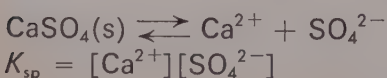
$$\frac{1000 \text{ g/liter}}{18 \text{ g/mole}} = 55.5 \text{ moles/liter}$$

- If the molecules of CH_3COOH and H_2O are assumed to have the same size, then 0.1 mole/liter CH_3COOH will replace 0.1 mole/liter H_2O . Thus $55.5 - 0.1 = 55.4$ moles of H_2O will be present in 1 liter of 0.10 *M* CH_3COOH solution.

Exercise 13-5

Write the equation for the dissolving of calcium sulfate, CaSO_4 . Write the solubility product expression.

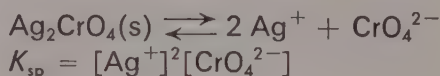
Answer



Exercise 13-6

Write the equation for the dissolving of silver chromate, Ag_2CrO_4 . Write the solubility product expression. Silver chromate dissolves to give Ag^+ and CrO_4^{2-} ions.

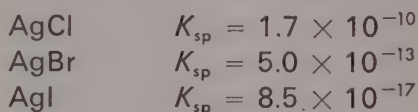
Answer



Exercise 13-7

Compare the K_{sp} values for AgCl , AgBr , and AgI . Which of these compounds is most soluble in water? Which is least soluble?

Answer

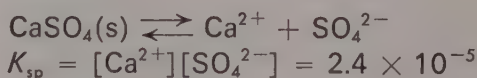


AgCl has the largest K_{sp} ; it is the most soluble. AgI is least soluble and has the smallest value of the solubility product.

Exercise 13-8

Calculate the solubility, in moles per liter, of calcium sulfate in water, using the solubility product given in Table 13-6.

Answer



If s moles dissolve in one liter of solution, then

$$\begin{aligned} [\text{Ca}^{2+}] &= [\text{SO}_4^{2-}] = s \\ (s)(s) &= 2.4 \times 10^{-5} \\ s &= \sqrt{2.4 \times 10^{-5}} = 4.9 \times 10^{-3} \text{ mole/liter} \end{aligned}$$

Exercise 13-9

A 50 ml volume of 0.04 *M* $\text{Ca}(\text{NO}_3)_2$ solution is added to 150 ml of 0.008 *M* $(\text{NH}_4)_2\text{SO}_4$ solution. Show that a trial value of the ion product for calcium sulfate is 6×10^{-5} . Will a precipitate form?

Answer

The Ca^{2+} ion concentration will be $\frac{1}{4}$ the initial value because the mixed volume is four times that in the $\text{Ca}(\text{NO}_3)_2$ solution. The SO_4^{2-} concentration will be $\frac{3}{4}$ times as large as it was originally.

$$[\text{Ca}^{2+}] = 0.04 \times \frac{1}{4} = 0.01 \text{ mole/liter}$$

$$[\text{SO}_4^{2-}] = 0.008 \times \frac{3}{4} = 0.006 \text{ mole/liter}$$

Trial ion product = $(0.01)(0.006) = 6 \times 10^{-5}$. This is larger than K_{sp} (2.4×10^{-5}) so a precipitate will form.

Problem 1

Sugar is added to a cup of coffee until no more sugar will dissolve. Does addition of another spoonful of sugar increase the rate at which the sugar molecules leave the crystal phase and enter the liquid phase? Will the sweetness of the liquid be increased by this addition? Explain.

Answer

The addition increases the area of solid, hence it does increase the rate at which molecules dissolve. The sweetness of the liquid is *not* increased, however, because the added solid increases the rate at which molecules leave the solution by the same amount that it increases the rate at which they enter the solution. Equilibrium is unaffected by the added solid.

Problem 2

Is equilibrium established in a fire burning in a fireplace? Explain.

Answer

No. There are many observable changes so equilibrium does not exist. Air is entering, while heat and smoke are leaving the system. Equilibrium is only attained in a closed system.

Problem 3

What, specifically, is "equal" in a chemical reaction that has attained a state of equilibrium?

Answer

The rate at which products are being formed equals the rate at which they are being consumed in the reverse reaction. Of course, a similar statement applies to reactants.

Problem 4

One drop of water may or may not establish a state of vapor pressure equilibrium when placed in a closed bottle. Explain.

Answer

Whether equilibrium is established depends upon the size of the bottle. In a small bottle at ordinary

temperature and pressure, equilibrium could probably be established without evaporation of the entire drop. In a large bottle, however, the space above the drop might never become saturated with water vapor before the whole drop evaporated. Hence there would be no liquid present, and liquid-vapor equilibrium would not be reached.

Problem 5

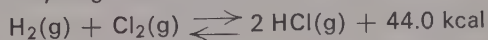
Why are chemical equilibria referred to as "dynamic?"

Answer

Chemical equilibria are referred to as "dynamic" because they are achieved by a balance between a forward and a reverse reaction. At equilibrium the two reactions are still going on, with the result that the chemicals on either side of the double arrow are being made as fast as they are being used. This might be contrasted to a static equilibrium; e.g., a book on a desk. The desk is pushing on the book and vice versa, but there is no exchange of position or conversion of one into the other.

Problem 6

The following chemical equation represents the reaction between hydrogen and chlorine to form hydrogen chloride:



- List four important pieces of information conveyed by this equation.
- What are three important areas of interest concerning this reaction for which no information is indicated?

Answer

- The equation tells us that:

- One mole H_2 reacts with 1 mole Cl_2 to yield 2 moles HCl (1 molecule H_2 + 1 molecule Cl_2 gives 2 molecules HCl).
- It represents an equilibrium reaction.
- All reacting substances in the system are in the gaseous state.
- The reaction is exothermic, liberating 44.0 kcal or 22 kcal/mole of $\text{HCl}(\text{g})$ formed.

- The equation does not give a clue about:

- The equilibrium concentrations.
- The rate at which equilibrium is reached.
- The reaction mechanism.

Problem 7

Each of the following systems has come to equilibrium.

Reaction	Added Reagent
(a) $\text{C}_2\text{H}_6(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{C}_2\text{H}_4(\text{g})$	$\text{H}_2(\text{g})$
(b) $\text{Cu}^{2+}(\text{aq}) + 4 \text{NH}_3(\text{aq}) \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$	$\text{CuSO}_4(\text{s})$
(c) $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightleftharpoons \text{AgCl}(\text{s})$	$\text{AgCl}(\text{s})$
(d) $\text{PbSO}_4(\text{s}) + \text{H}^+(\text{aq}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + \text{HSO}_4^-(\text{aq})$	$\text{Pb}(\text{NO}_3)_2$ solution
(e) $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{heat}$	heat

Answer

- (a) C_2H_6 (increase); H_2 (increase); C_2H_4 (decrease).
 (b) Cu^{2+} (increase); NH_3 (decrease); $\text{Cu}(\text{NH}_3)_4^{2+}$ (increase).
 (c) Ag^+ (no change); Cl^- (no change); AgCl (no change).
 (d) PbSO_4 (no change in concentration; the amount of solid would increase); $\text{H}^+(\text{aq})$ (increase); Pb^{2+} (increase); HSO_4^- (decrease).
 (e) CO (increase); O_2 (increase); CO_2 (decrease).

What would be the effect on the equilibrium concentration (increase, decrease, no change) of each substance in the system when the listed reagent is added?

Notice that an important point is made in this problem that deserves discussion. For example, in question (a), the addition of H_2 shifts the equilibrium so as to *partially* counteract the imposed change. Thus the equilibrium will shift to consume *some* of the added H_2 *but never all*. Hence there is a net *increase* in H_2 pressure, though not as much as there would have been had a new equilibrium not been established as predicted by Le Chatelier's Principle. The consumption of H_2 is shown, of course, in the decrease of C_2H_4 and in the increase of C_2H_6 .

Problem 8

The reaction $\text{CO}(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{NO}(\text{g})$ is exothermic, with $\Delta H = -54.1$ kcal/mole. What happens in this system at equilibrium if;

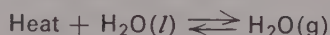
- (a) the temperature is increased?
 (b) the volume is decreased by a factor of ten?

Answer

- (a) CO_2 and NO would react to give $\text{CO} + \text{NO}_2$, using some of the added energy.
 (b) No effect; neither forward nor reverse reaction cause a change in number of moles.

Problem 9

If the phase change represented by



has reached equilibrium in a closed system:

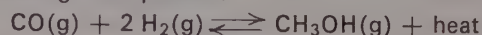
- (a) What will be the effect of a reduction of volume, thus increasing the pressure?
 (b) What will be the effect of an increase in temperature?
 (c) What will be the effect of injecting some steam into the closed system, thus raising the pressure?

Answer to Problem 9

- (a) The reverse reaction is favored. $\text{H}_2\text{O}(\text{g})$ goes to $\text{H}_2\text{O}(\text{l})$, reducing the volume to counteract increased pressure. In this case the pressure is reduced to the starting value.
 (b) Forward reaction favored. The $\text{H}_2\text{O}(\text{l})$ goes to $\text{H}_2\text{O}(\text{g})$, absorbing heat to counteract increased temperature.
 (c) The reverse reaction is favored, just as in (a).

Problem 10

Methanol (methyl alcohol) can be made according to the following net equation:



Predict the effect on equilibrium concentrations of an increase in:

- (a) Temperature. (b) Pressure.

Answer

- (a) According to Le Chatelier's Principle, an increase in the temperature of a system at equilibrium will, cause a change that tends

to partially counteract the increased temperature. Hence some CH_3OH will decompose to CO and H_2 , absorbing heat.

- (b) Again, according to Le Chatelier's Principle, new equilibrium concentrations will form so as to partially undo the change imposed on the system. More CH_3OH will form if the pressure is increased. The formation of one mole (CH_3OH) from 3 moles ($\text{CO} + 2 \text{H}_2$) will tend to reduce the pressure.

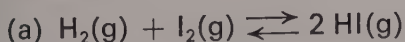
Problem 11

Consider two separate closed systems, each at equilibrium:

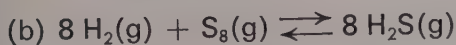
- (a) HI and the elements from which it is formed.
 (b) H_2S and the elements from which it is formed.

What would happen in each system if the total pressure were increased? Assume that conditions are such that all reactants and products are gases.

Answer



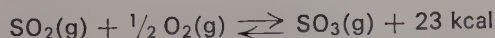
Since the number of moles of reactants equals the number of moles of product, pressure will have no effect on equilibrium concentrations.



Since nine moles of reactants produce only eight moles of product, an increase in pressure will produce more $\text{H}_2\text{S}(\text{g})$. Of course, at sufficiently high temperatures, $\text{S}_8(\text{g})$ breaks apart, eventually to $\text{S}(\text{g})$, but the reaction between $\text{H}_2(\text{g})$ and $\text{S}(\text{g})$ gives the same pressure effect.

Problem 12

Given:



- (a) Discuss the conditions that favor a high equilibrium concentration of SO_3 .
 (b) How many grams of oxygen gas are needed to form 1.00 gram of SO_3 ?

Answer

- (a) High pressure. All substances are gaseous, and there are $1\frac{1}{2}$ moles on the left compared to one mole on the right.
 High concentration of SO_2 and/or oxygen.

Low temperature. Since this reaction is exothermic, lowering the temperature favors a greater equilibrium concentration of $\text{SO}_3(\text{g})$, for this change produces heat to counteract the lowered temperature.

(b) $\left(\frac{1.00 \text{ g SO}_3}{80 \text{ g/mole}} \right) = 0.0125 \text{ mole SO}_3$

One mole of SO_3 requires $\frac{1}{2}$ mole of O_2 .

$$(0.0125 \text{ mole}) \left(\frac{1}{2} \right) (32 \text{ g O}_2/\text{mole}) = 0.200 \text{ g O}_2$$

Problem 13

How does a catalyst affect the equilibrium conditions of a chemical system?

Answer

A catalyst has no effect upon the equilibrium conditions but affects only the rate at which such conditions are reached.

Problem 14

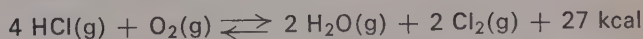
In any discussion of chemical equilibrium why are concentrations expressed in moles, rather than in grams, per unit volume?

Answer

Moles express concentration in terms of the number of reacting particles. One mole of various reactants can be compared directly, since one mole of any reactant contains the same number of particles. One-gram portions of several reactants do not have an equal number of particles.

Problem 15

Consider the reaction:



What effect would the following changes have on the equilibrium concentration of $\text{Cl}_2(\text{g})$? Give reasons for each answer.

- (a) Increasing the temperature of the reaction vessel.
 (b) Decreasing the total pressure.
 (c) Increasing the concentration of O_2 .
 (d) Increasing the volume of the reaction chamber.
 (e) Adding a catalyst.

Answer

- (a) The Cl_2 concentration decreases. Concen-

trations shift so as to absorb heat. This causes some Cl_2 to react with H_2O to form HCl and O_2 , consuming Cl_2 .

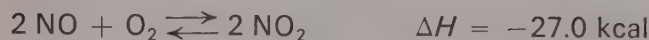
- (b) Decreases. Concentrations shift so as to increase pressure. To do this, the products change to reactants in a mole ratio of 4/5. This consumes Cl_2 .
- (c) Increases. Concentrations shift so as to consume some of the added O_2 , producing more Cl_2 .
- (d) Decreases. Pressure is reduced, hence the answer to (b) is applicable.
- (e) No change. A catalyst changes the rate at which equilibrium concentrations are reached, but not the concentrations themselves.

Problem 16

Nitric oxide, NO , releases 13.5 kcal/mole when it reacts with oxygen to give nitrogen dioxide. Write the equation for this reaction and predict the effect of (i) raising the temperature, and of (ii) increasing the concentration of NO (at a fixed temperature) on:

- (a) the equilibrium concentrations;
 (b) the numerical value of the equilibrium constant;
 (c) the speed of formation of NO_2 .

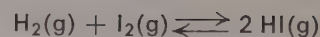
Answer



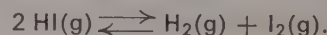
- (a) (i) Since the reaction is exothermic, increasing temperature will favor greater concentration of NO and O_2 at equilibrium.
- (ii) Increasing NO will favor an increase in the concentration of NO_2 and a decrease in O_2 at equilibrium.
- (b) (i) The numerical value of K changes with temperature; since increasing the temperature favors reactants, it must lower the value of K .
- (ii) Increasing the concentration of NO favors the forward reaction but does not alter the numerical value of K for a given reaction.
- (c) (i) Increasing the temperature increases the rate of formation of NO_2 .
- (ii) Increasing the concentration of NO increases the rate of formation of NO_2 .

Problem 17

Given:



At 450°C , $K = 50.0$ for this reaction. Calculate the equilibrium constant at 450°C if the reaction is written:



Answer

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 50.0 \text{ (forward reaction)}$$

$$K = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{1}{50.0} = 0.0200 \text{ (reverse reaction)}$$

Problem 18

Write the equilibrium expression for the following reactions.

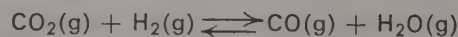
- (a) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 (b) $\text{CO}(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{NO}(\text{g})$
 (c) $\text{Zn}(\text{s}) + 2\text{Ag}^+(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$
 (d) $\text{PbI}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{I}^-(\text{aq})$
 (e) $\text{CN}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCN}(\text{aq}) + \text{OH}^-(\text{aq})$

Answer

- (a) $K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$
 (b) $K = \frac{[\text{CO}_2][\text{NO}]}{[\text{NO}_2][\text{CO}]}$
 (c) $K = \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$
 (d) $K = [\text{Pb}^{2+}][\text{I}^-]^2$
 (e) $K = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$

Problem 19

The water gas reaction



was carried out at 900°C with the following results.

Trial Number	Partial Pressure, Atm. at Equilibrium			
	CO	H ₂ O	CO ₂	H ₂
1	0.352	0.352	0.648	0.148
2	0.266	0.266	0.234	0.234
3	0.186	0.686	0.314	0.314

- (a) Write the equilibrium law expression.
 (b) Verify that the expression in (a) is a constant, using the data given. See Prob. 20.

Answer to Problem 19

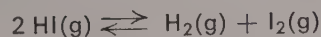
$$(a) K = \frac{[P_{CO}][P_{H_2O}]}{[P_{CO_2}][P_{H_2}]}$$

(b) Trial 1; $K = 1.291$.Trial 2; $K = 1.290$.Trial 3; $K = 1.293$.

To the significant figures consistent with the data, these are all equal to 1.29.

Problem 20

In the reaction



at 448°C the partial pressures of the gases at equilibrium are as follows:

partial pressure of HI = 4.0×10^{-3} atm;

partial pressure of H_2 = 7.5×10^{-3} atm;

partial pressure of I_2 = 4.3×10^{-5} atm.

When pressures are properly used in the equilibrium expression, a constant is obtained. What is that constant for this reaction?

Answer

$$K = \frac{(7.5 \times 10^{-3})(4.3 \times 10^{-5})}{(4.0 \times 10^{-3})^2} = 0.02$$

$$= 2.0 \times 10^{-2}$$

Problem 21

Reactants A and B are mixed, each at a concentration

of 0.80 mole/liter. They react slowly, producing C and D : $A + B \rightleftharpoons C + D$. When equilibrium is reached, the concentration of C is measured and found to be 0.60 mole/liter. Calculate the value of the equilibrium constant.

Answer: $K = 9.0$.

Answer

$$K = \frac{[C][D]}{[A][B]}$$

$$[C] = 0.60 \text{ mole/liter} = [D]$$

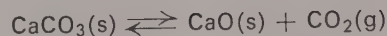
$$[A] = 0.80 - 0.60 = 0.20 \text{ mole/liter}$$

$$[B] = 0.80 - 0.60 = 0.20 \text{ mole/liter}$$

$$K = \frac{[0.60][0.60]}{[0.20][0.20]} = 9.0$$

Problem 22

Given:



At a fixed temperature, what effect would adding more CaCO_3 have on the concentration of CO_2 in the region above the solid phase? Explain.

Answer

None. The K for this reaction depends only upon the concentration of CO_2 , as long as temperature does not change and as long as both CaCO_3 and CaO are present. It does not depend upon how much solid is present.

Problem 23

Equilibrium constants are given for several systems below.

Reaction	K
(a) $\text{CH}_3\text{COOH(aq)} \rightleftharpoons \text{H}^+\text{(aq)} + \text{CH}_3\text{COO}^-\text{(aq)}$	1.8×10^{-5}
(b) $\text{CdS(s)} \rightleftharpoons \text{Cd}^{2+}\text{(aq)} + \text{S}^{2-}\text{(aq)}$	7.1×10^{-28}
(c) $\text{H}^+\text{(aq)} + \text{HS}^-\text{(aq)} \rightleftharpoons \text{H}_2\text{S(aq)}$	1×10^7

In which case does the reaction as written occur to the greatest extent?

Answer

Only in reaction (c) is the K greater than 1, and hence this reaction occurs to the greatest extent. Such a large K indicates a considerable concentration of products as compared

to reactants at equilibrium. All the other K 's given indicate that product concentrations are much less than reactant concentrations at equilibrium.

Problem 24

Write the solubility product expression for each of the following reactions.

- (a) $\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$
 (b) $\text{Zn}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$
 (c) $\text{Ca}_3(\text{PO}_4)_2(\text{s}) \rightleftharpoons 3\text{Ca}^{2+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq})$

Answer

- (a) $K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$
 (b) $K_{\text{sp}} = [\text{Zn}^{2+}][\text{OH}^{-}]^2$
 (c) $K_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$

Problem 25

Write the solubility product expression for each of the following substances in water.

- (a) calcium carbonate.
 (b) silver sulfide.
 (c) aluminum hydroxide.

Answer

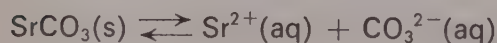
- (a) $K_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$
 (b) $K_{\text{sp}} = [\text{Ag}^{+}]^2[\text{S}^{2-}]$
 (c) $K_{\text{sp}} = [\text{Al}^{3+}][\text{OH}^{-}]^3$

Problem 26

Experiments show that 0.0059 gram of SrCO_3 will dissolve in 1.0 liter of water at 25°C . What is K_{sp} for SrCO_3 ?

Answer: 1.6×10^{-9} .

Answer



For every mole dissolved, one mole of Sr^{2+} ions and one mole of CO_3^{2-} ions are formed.

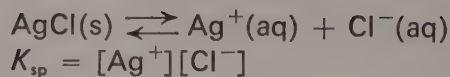
$$\begin{aligned}\text{Moles SrCO}_3(\text{s}) \text{ dissolved} &= \frac{0.0059 \text{ g/liter}}{148 \text{ g/mole}} \\ &= 4.0 \times 10^{-5} \text{ mole/liter}\end{aligned}$$

$$\begin{aligned}K_{\text{sp}} &= [\text{Sr}^{2+}][\text{CO}_3^{2-}] = (4.0 \times 10^{-5})^2 \\ &= 1.6 \times 10^{-9}\end{aligned}$$

Problem 27

The solubility product of AgCl is 1.4×10^{-4} at 100°C . Calculate the solubility of silver chloride in boiling water.

Answer



but here

$$\begin{aligned}[\text{Ag}^{+}] &= [\text{Cl}^{-}] \\ [\text{Ag}^{+}]^2 &= 1.4 \times 10^{-4} \\ [\text{Ag}^{+}] &= \sqrt{1.4 \times 10^{-4}} = 1.2 \times 10^{-2} M \\ \text{Solubility} &= 1.2 \times 10^{-2} M\end{aligned}$$

Problem 28

How many milligrams of silver bromide dissolve in 20 liters of water? (Use the data given in Table 13-6.)

Answer

$$\begin{aligned}\text{AgBr}(\text{s}) &\rightleftharpoons \text{Ag}^{+}(\text{aq}) + \text{Br}^{-}(\text{aq}) \\ K_{\text{sp}} &= [\text{Ag}^{+}][\text{Br}^{-}] = 5.0 \times 10^{-13} = 50 \times 10^{-14} \\ [\text{Ag}^{+}] &= [\text{Br}^{-}] \\ [\text{Ag}^{+}]^2 &= 50 \times 10^{-14} \\ [\text{Ag}^{+}] &= 7.0 \times 10^{-7} M \\ \text{In 20 liters, there will be } &20 \times 7.0 \times 10^{-7} \\ &= 1.4 \times 10^{-5} \text{ mole AgBr.} \\ \text{In 20 liters, there will be } &(1.4 \times 10^{-5} \text{ mole}) \\ &\times (188 \text{ g/mole}) = 2.63 \times 10^{-3} \text{ gram AgBr.} \\ \text{In 20 liters, 2.63 milligrams AgBr dissolve.}\end{aligned}$$

Problem 29

Suppose you add 0.002 mole of solid $\text{Pb}(\text{NO}_3)_2$ to one liter of $0.001 M \text{H}_2\text{SO}_4$. As the lead nitrate dissolves, will lead sulfate precipitate?

Answer

$$\begin{aligned}\text{PbSO}_4(\text{s}) &\rightleftharpoons \text{Pb}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \\ K_{\text{sp}} &= [\text{Pb}^{2+}][\text{SO}_4^{2-}] = 1.3 \times 10^{-8} \\ [\text{Pb}^{2+}] &= \frac{0.002 \text{ mole}}{\text{liter}} \\ [\text{SO}_4^{2-}] &= \frac{0.001 \text{ mole}}{\text{liter}}\end{aligned}$$

If all the $\text{Pb}(\text{NO}_3)_2$ dissolves, the trial product of ion concentrations is

$$(2 \times 10^{-3})(1 \times 10^{-3}) = 2 \times 10^{-6}$$

This is *larger* than K_{sp} ; hence these concentrations cannot continue to exist; some $\text{PbSO}_4(\text{s})$ will precipitate, removing ions until the actual product of ion concentrations equals K_{sp} .

Problem 30

Suppose 10 ml of 1.0 *M* AgNO₃ is diluted to one liter with tap water. If the chloride concentration in the tap water is about 10⁻⁵ *M*, will a precipitate form?

Answer

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.7 \times 10^{-10}$$

$$[\text{Ag}^+] = \frac{(0.010 \text{ liter})(1.0 \text{ mole/liter})}{1.0 \text{ liter}} = 0.010 \text{ } M$$

$$[\text{Cl}^-] = 10^{-5} \text{ } M$$

Trial product: $[\text{Ag}^+][\text{Cl}^-] = (10^{-2})(10^{-5}) = 10^{-7}$. This exceeds $K_{sp} = 1.7 \times 10^{-10}$. Hence a precipitate will form.

Problem 31

The test described in Problem 30 does *not* give a precipitate if laboratory distilled water is used. What is the maximum chloride concentration that could be present?

Answer

A precipitate will form if the chloride concentration exceeds the value which makes the product $[\text{Ag}^+][\text{Cl}^-]$ equal to K_{sp} .

$$[\text{Ag}^+] = 1.0 \times 10^{-2}$$

$$[\text{Cl}^-] = \frac{K_{sp}}{[\text{Ag}^+]} = \frac{1.7 \times 10^{-10}}{1.0 \times 10^{-2}} = 1.7 \times 10^{-8}$$

$[\text{Cl}^-]$ cannot exceed $1.7 \times 10^{-8} \text{ } M$ in the distilled water.

Problem 32

Will a precipitate exist at equilibrium if 0.5 liter of $2 \times 10^{-3} \text{ } M$ AlCl₃ solution and 0.5 liter of $4 \times 10^{-2} \text{ } M$ sodium hydroxide solution are mixed and diluted to 10³ liters with water at room temperature?

$$K_{sp} \text{ of Al(OH)}_3 \text{ is } = 5 \times 10^{-33}$$

Answer

Half a liter of $2 \times 10^{-3} \text{ } M$ AlCl₃ contains 1×10^{-3} mole of Al³⁺.

$$[\text{Al}^{3+}] = \frac{1 \times 10^{-3}}{10^3} = 1 \times 10^{-6} \text{ } M$$

Half a liter of $4 \times 10^{-2} \text{ } M$ NaOH contains 2×10^{-2} mole of OH⁻.

$$[\text{OH}^-] = \frac{2 \times 10^{-2}}{10^3} = 2 \times 10^{-5} \text{ } M$$

$$[\text{Al}^{3+}][\text{OH}^-]^3 = (1 \times 10^{-6})(2 \times 10^{-5})^3 = 8 \times 10^{-21}$$

The solubility product for Al(OH)₃ is 5×10^{-33} , which is much smaller than 8×10^{-21} , thus a precipitate will form.

Problem 33

Select from each of the following pairs the more random system.

- A brand new deck of cards arranged according to suit and number.
The same deck of cards after shuffling.
- A box full of sugar cubes.
Sugar cubes thrown on the floor.
- A haystack.
Stacked firewood.

Answer

- The shuffled deck.
- Cubes on the floor.
- A haystack.

Problem 34

For each of the following reactions, state: (i) whether tendency toward minimum energy favors reactants or products, (ii) whether tendency toward maximum randomness favors reactants or products.

- $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(s) \quad \Delta H = -1.4 \text{ kcal}$
- $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g) \quad \Delta H = +10 \text{ kcal}$
- $\text{CaCO}_3(s) + 43 \text{ kcal} \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$
- $\text{I}_2(s) + 1.6 \text{ kcal} \rightleftharpoons \text{I}_2(\text{in alcohol})$
- $4 \text{ Fe}(s) + 3 \text{ O}_2(g) \rightleftharpoons 2 \text{ Fe}_2\text{O}_3(s) + 400 \text{ kcal}$

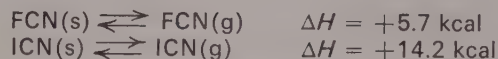
Answer

- (i) Product;
(ii) reactant.
- (i) Reactant;
(ii) product.
- (i) Reactants;
(ii) products (because of randomness of gas).
- (i) Reactant;
(ii) product (because of randomness of solution).
- (i) Products;
(ii) reactants (because of randomness of gas).

Stress that these tendencies are opposite. Thus when one favors reactants, the other will favor products.

Problem 35

When a solid evaporates directly (without melting), the process is called *sublimation*. Evaporation of solid CO_2 is a familiar example. Two other substances that sublime are FCN and ICN:



- In sublimation, does the tendency toward maximum randomness favor solid or gas?
- In sublimation, does the tendency toward minimum energy favor solid or gas?
- In view of part b, would you expect solid ICN to have a lower or higher vapor pressure than solid FCN at the same temperature?

Answer

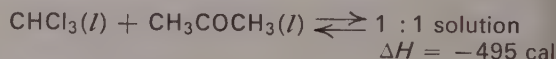
- A gas is more random than a solid. Randomness favors the gas phase.
- Heat is absorbed during sublimation. Minimum energy favors the solid phase.
- Since solid ICN is more favored by ΔH than is solid FCN, the equilibrium vapor pressure will be lower. The randomness effects are about the same at equal pressures. In fact, the vapor pressure of solid ICN reaches 760 mm only after the temperature is raised to 413°K.

Problem 36

Liquid chloroform, CHCl_3 , and liquid acetone, CH_3COCH_3 ,

dissolve in each other in all proportions (they are said to be miscible).

- When pure CHCl_3 is mixed with pure acetone, is randomness increased or decreased?
- Does the tendency toward maximum randomness favor reactants or products in the reaction



- Considering the sign of ΔH in part b, does the tendency toward minimum energy favor reactants or products?
- In view of your answers to parts b and c, discuss the experimental fact that these two liquids are miscible.

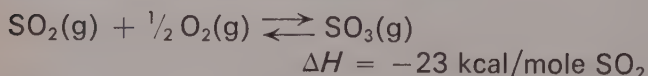
Answer

- Since two kinds of molecules are mixed in the solution, it is more random than the pure liquids, each of which consists of only one kind of liquid.
- Tendency toward maximum randomness favors the more random state, the solution.
- $\Delta H = -495$. The negative sign means heat is evolved. Hence, the tendency toward minimum energy favors products.
- The fact that the two liquids dissolve in all proportions is consistent with the fact that tendencies to maximum randomness and minimum energy work together, *both* favoring the solution.

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

Questions 1–7 are based on the following reaction, which takes place in a closed container in the presence of a suitable catalyst.



- How does the rate of the forward reaction compare to the rate of the reverse reaction at equilibrium?

Answer: They are the same.

- What is the effect of adding some additional $\text{SO}_2(\text{g})$ after the system has reached equilibrium?

Answer

The addition of more $\text{SO}_2(\text{g})$ destroys the existing equilibrium, causing the system to change; the $\text{SO}_3(\text{g})$ concentration is increased, and the $\text{O}_2(\text{g})$ concentration is decreased until a new equilibrium state is established.

- If the pressure of the system is increased by reducing the volume (temperature and

amounts of gases remaining constant) the pressure of each component goes up. How will the equilibrium shift, and what further effect will this have on the $\text{SO}_3(\text{g})$ concentration? Why?

Answer

The $\text{SO}_3(\text{g})$ concentration would be still higher after the new equilibrium is established. According to Le Chatelier's Principle, the system will shift to compensate for the disturbing factor. In this situation, increasing the pressure favors the reaction which tends to reduce the pressure. Relatively speaking, there are $1\frac{1}{2}$ volumes of reactants to one volume of product. The formation of more $\text{SO}_3(\text{g})$ would have the effect of relieving some of the added pressure but increases the $\text{SO}_3(\text{g})$ pressure still more.

4. What effect should increasing the temperature have on this reaction if pressure remains constant?

Answer

Since the reaction producing $\text{SO}_3(\text{g})$ is exothermic, an increase in temperature should cause a new equilibrium, with more $\text{SO}_2(\text{g})$ and $\text{O}_2(\text{g})$ present at equilibrium than before.

5. What effect does a catalyst have on the rate of the forward reaction?

Answer

A catalyst increases the rate of the forward reaction.

6. What effect does a catalyst have on the rate of the reverse reaction?

Answer

A catalyst increases the rate of the reverse reaction.

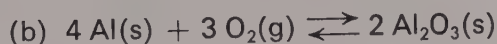
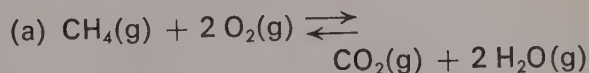
7. Compare the equilibrium concentration of $\text{SO}_3(\text{g})$ without a catalyst to the equilibrium concentration of $\text{SO}_3(\text{g})$ with a catalyst. Explain.

Answer

They are the same. The presence of a

catalyst increases the rates of reaction but does not alter the equilibrium concentrations.

8. Write the equilibrium law relations for the following reactions.



Answer

$$(a) K = \frac{[\text{CO}_2][\text{H}_2\text{O}]^2}{[\text{CH}_4][\text{O}_2]^2}$$

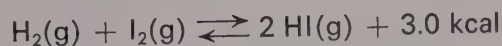
$$(b) K = \frac{1}{[\text{O}_2]^3}$$

9. A large number of pennies is arranged with each coin heads-up in a box. The box is closed and shaken. Predict what will be found when the box is opened. Explain.

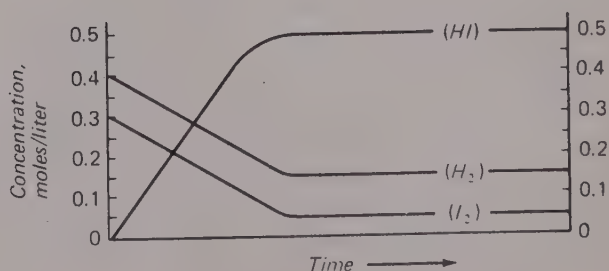
Answer

Many coins will show tails when the box is opened. The tendency toward maximum randomness favors a disorderly arrangement, and the various arrays have about the same energy requirements.

Questions 10–14 relate to the following diagram, which shows how the concentration of each of the products and reactants changes as the reaction



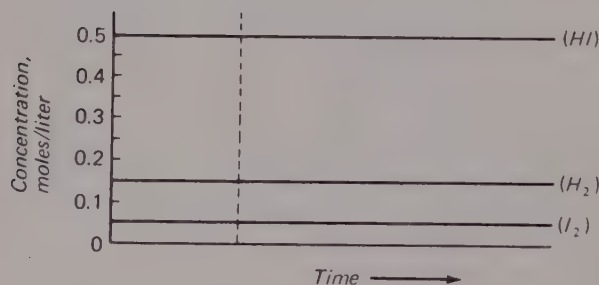
proceeds until equilibrium is finally established for temperature T_1 and pressure P_1 .



For each of questions 10–12, choose, from the descriptions I–V, those which best describe the chart represented in each question. In each case the system is initially at equilibrium, but at the time marked by the broken line some change in condition is made.

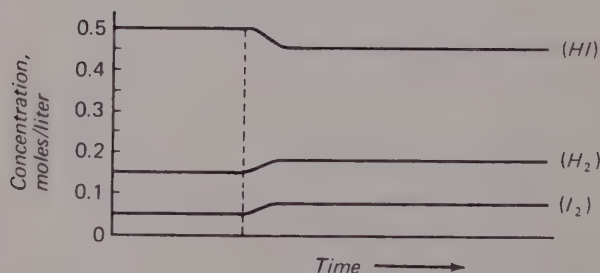
- I. The temperature is increased to T_2 while the pressure is maintained at P_1 .
- II. The temperature is increased to T_2 , and the pressure is increased to P_2 by adding an inert gas.
- III. H_2 is added to the system (T_1 and P_1 maintained).
- IV. The total pressure is increased to P_2 by adding an inert gas while the temperature is maintained at T_1 .
- V. A catalyst is added to the system with all other factors remaining constant.

10.



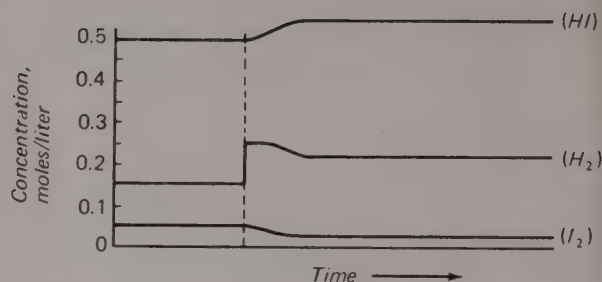
Answer: IV and V.

11.



Answer: I and II.

12.



Answer: III.

13. Which of the following will change the value of the equilibrium constant for the reaction between $H_2(g)$ and $I_2(g)$?

- (1) Adding a catalyst;
- (2) Increasing the pressure (temperature constant);
- (3) Increasing the temperature;
- (4) Increasing the concentration of the reactants;
- (5) Increasing the concentration of the products.

Answer: (3).

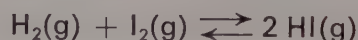
14. Calculate the value of the equilibrium constant for the reaction. Use the equilibrium concentrations given in the first chart.

Answer

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{(5 \times 10^{-1})^2}{(0.15)(0.05)} = 33$$

15. What mass of $HI(g)$ is formed in a mixture of 0.10 mole of $H_2(g)$ and 0.20 mole of $I_2(g)$? Temperature and pressure are such that 20% of the H_2 is converted into HI .

Answer



The equation shows that H_2 and I_2 react in the molar ratio of 1/1.

$$\text{Moles of } H_2 \text{ reacting} = (0.10)(0.20) = 0.020$$

Moles of HI formed

$$= (0.020 \text{ mole H}_2) \left(\frac{2 \text{ moles HI}}{1 \text{ mole H}_2} \right) = 0.040$$

$$(0.040 \text{ mole HI}) \left(129 \frac{\text{g}}{\text{mole HI}} \right)$$

$$= 5.16 \text{ g HI or } 5.2 \text{ g}$$

Given $2 \times 10^{-3} M$ solutions of $\text{Pb}(\text{NO}_3)_2$ and Na_2SO_4 , determine the following:

16. Would you expect a precipitate to form when equal volumes of the two solutions are mixed? ($K_{sp} = 1.3 \times 10^{-8}$.)

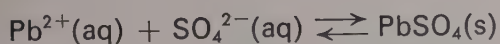
Answer: Yes.

$$[\text{Pb}^{2+}][\text{SO}_4^{2-}] = (1 \times 10^{-3})(1 \times 10^{-3}) = 1 \times 10^{-6}$$

17. A precipitate is expected to form when the product of the maximum possible ion concentrations is greater than the K_{sp} .

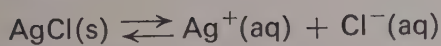
Write an equilibrium equation for the most probable reaction when equal volumes of the two solutions are mixed together.

Answer



18. What is the equilibrium concentration of Ag^+ ions in a saturated aqueous solution of AgCl made by shaking AgCl with water? ($K_{sp} \approx 1 \times 10^{-10}$.) Show calculations.

Answer

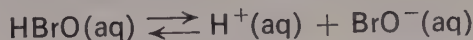


$$1 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-]$$

$$[\text{Ag}^+] = [\text{Cl}^-] = \sqrt{1 \times 10^{-10}}$$

$$[\text{Ag}^+] = 1 \times 10^{-5} M$$

19. The equilibrium constant for the reaction,



is 2×10^{-9} . Determine the $[\text{H}^+]$ in a $0.05 M$ solution of hypobromous acid, HBrO .

Answer

$$K = \frac{[\text{H}^+][\text{BrO}^-]}{[\text{HBrO}]} = 2 \times 10^{-9}$$

Let

$$y = [\text{H}^+] = [\text{BrO}^-]$$

Then

$$0.05 - y = [\text{HBrO}]$$

and

$$\frac{y^2}{0.05 - y} = 2 \times 10^{-9}$$

Since y is likely to be small compared to 0.05 we will neglect it. Then

$$y^2 = (2 \times 10^{-9})(5 \times 10^{-2}) = 10 \times 10^{-11}$$

$$y = (1 \times 10^{-10})^{1/2} = 1 \times 10^{-5} \text{ mole/liter}$$

which is indeed small compared to 0.05 .

20. Write the solubility product expression for the dissolution of each of the following solids.

(1) PdS ,

(2) Ag_3PO_4 ,

(3) chromic carbonate,

(4) gallium hydroxide.

Answer

$$(1) K_{sp} = [\text{Pd}^{2+}][\text{S}^{2-}].$$

$$(2) K_{sp} = [\text{Ag}^+]^3[\text{PO}_4^{3-}].$$

$$(3) K_{sp} = [\text{Cr}^{3+}]^2[\text{CO}_3^{2-}]^3.$$

$$(4) K_{sp} = [\text{Ga}^{3+}][\text{OH}^-]^3.$$

Intent and Approach

This chapter continues the discussion of equilibrium, now applied to the important and complementary classes: acids and bases. After first establishing the difference between strong and weak electrolytes, we take up the ionization of water and the special role of $\text{H}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$ —all in terms of dynamic equilibrium. We then give the experimental, or operational, definition of acids and bases, and consider a titration. Next we mention some broader aspects of

the behavior and definition of acids (Brønsted Theory). This material sets the stage for the treatment of acid strength, during which we use the equilibrium constant as a quantitative measure. Having gone through this chapter, a student should be able to calculate $\text{H}^+(\text{aq})$ from a given $\text{OH}^-(\text{aq})$, or vice versa, and to work problems involving the relationship between K_A , hydrogen ion, and acid concentrations.

Outline

Operational and conceptual definitions are illustrated and contrasted (14-1).

The four characteristic properties of acids given in Section 14-1 are related to the release of $\text{H}^+(\text{aq})$ ions. The distinguishing properties of bases are listed and explained as a reaction with H^+ . This view is called the Arrhenius definition.

Water is shown to be a weak electrolyte and the ion product, K_w , is introduced (14-3).

The study of ionic equilibrium in water and of how it is shifted by the addition of ion-producing solutes reveals the role of H^+ and OH^- (14-4).

Through the use of the reaction between H^+

and OH^- the equilibrium calculations are extended to acid-base reactions or titrations (14-5).

The Brønsted-Lowry definition of acids as a competition for protons provides a broader generalization (14-6) and leads to a way to express the strength of acids (14-7). K_A is defined as a measure of relative strength.

An experimental method for determining K_A is given, and used to illustrate typical calculations (14-8, 14-9).

The trend of acidic or basic properties of third-row elements is touched on (14-10).

A review concludes the chapter (14-11).

New Concepts

1. Definition of a group of chemicals by properties of an ion common to all: acids as a source of $\text{H}^+(\text{aq})$.
2. The differences and advantages of conceptual

- and operational definitions.
3. Concentration changes during approach to neutralization: titration.
4. Acid and base strength.

SCHEDULE AND RELATED MATERIAL

Suggested Time : 10 days

Text Section	Topic and Other Work	Exercises	Problems		
			Easy	Medium	Hard
14-1	Operational Definitions of Acids and Bases		1	2, 3	
14-2	Arrhenius Definitions of Acids and Bases			4	
14-3	The Neutralization Reaction Expt. 31. Heat of Acid-Base Reactions Demo. 32. Electrical Conductivity of Acids and Bases Demo. 33. Titration	1, 2	5	6	
14-4	The Special Roles of H^+ and OH^- Expt. 32. Acid-Base Titration	3-5	7		8
14-5	Acid-Base Titrations	6, 7		9, 11-15	10
14-6	The Brønsted-Lowry Definition of Acids and Bases	8			
14-7	The Strengths of Acids and Bases	9, 10	16, 17, 19	18, 20, 21	22
14-8	Experimental Determination of K_A Expt. 33. Determination of $[H^+]$ Using Indicators			23, 27	24, 25
14-9	Calculations of $[H_3O^+]$ Film: Acid-Base Indicators			26	
14-10	Acidic and Basic Properties of Third-Row Elements			28	29
14-11	Review				

Development

14-1 Operational Definitions of Acids and Bases

One operation used to separate acids from some other chemicals should be demonstrated. Use the device described in Demonstration 19 (Lab Guide, p. 98) or review the results of Demonstration 21 (Lab Guide, p. 99). Show that there is ample evidence for the conductivity of acids (and bases), a property true for all ionic solu-

tions; it shows the presence of ions but doesn't identify acids or bases. The presence of ions is one facet of the definition. *Solutions of acids contain ions.*

You can show the liberation of hydrogen in a quick test. Along with the stated (not proved) fact that acids are found by analysis to contain hydrogen, this test helps establish that hydrogen (or its ion) is characteristic of all acids.

The litmus test is, of course, easy to show, but the color change results from a chemical change in a compound whose structure is too complex to show at this time. Moreover, it does not give directly any information about the nature of the acidic solution. Present it as a quick and easy test for acids. Here is a mnemonic device for remembering the color of litmus:

RED in ACID solution BLUE in BASIC solution

The typical taste of acids can be identified in vinegar (acetic acid) and sour milk (lactic acid). The statement about the taste of acids offers a basis for a short set of remarks about safety in the laboratory. Emphasize that tasting, or sometimes smelling, unknown substances is *not* for amateurs. Professionals use these tests with extreme caution.

Point out that this classification by operation is just what the child did in the analogy in Chapter 1. Notice that the analogy leads to a *postulate* which states that we can identify an acid by its ability to release protons. This is a conceptual definition. A great many tests of the postulate have been performed, and the results taken as a body establish the usefulness of the postulated description of an acid.

The same method is applied to bases and should go easily once the idea of describing and defining a chemical class by its properties is well planted in the student's mind.

One question that may arise is "Why are no acids formed by reaction with water—somewhat as Na_2CO_3 and NH_3 give bases?" Actually there are; SO_2 and CO_2 are examples of acid-forming compounds. The production of $\text{H}^+(\text{aq})$ is best postponed until Section 14-6. There is no need to go into a discussion of acidic and basic oxides as such. To do so would require more chemistry than the student has so far.

You may find it useful to contrast the two kinds of definitions, operational and conceptual, with an example independent of chemistry. This analogy is not in the Textbook.

Contrast the following pair of definitions.

- (1) A "star" is an athlete who regularly scores an unusually large number of points or who, in clever defensive acts, repetitiously and advantageously contributes to the welfare of his team.
- (2) A "star" is an athlete with unusual muscular coordination.

The first definition is "operational." It explicitly states criteria for deciding whether a player is a "star." He is one who "regularly scores an unusually large number of points" or who "in clever defensive acts, repetitiously and. . ." To decide if a player is a "star," you count his scoring or, alternatively, number the outstanding defensive plays he makes.

The second definition might be called a "conceptual definition." It offers an explanation of *why* the athlete enjoys special success in his sport. It is one step removed from things that show on the scoreboard.

The first definition gives no clue why one player is a "star" and another player is not. Its value is that it is practical, useful, and surely correct. It does not matter how awkward a basketball player is; if he scores 30 points per game he is assured of a considerable amount of public acclaim.

The value of the second (conceptual) definition is that it contains more information about "stardom." If accurate, it has the deeper significance. It might help the basketball coach more in developing the optimum characteristics of his squad. It permits him to *predict* athletic skill in advance of the first game.

Returning to our two definitions of an acid, the first, the operational definition, gives clear-cut instructions on how to decide whether a given substance is an acid. Dissolve it in water and see if it has certain properties. The second (conceptual) definition, however, has the deeper significance since it includes our knowledge of why an acid has these particular properties. It provides a basis for finding hidden likenesses between acid-base reactions in water and other reactions in other solvents. Each type of definition has its merit; neither is *the* definition.

14-2 The Arrhenius Definitions of Acids and Bases

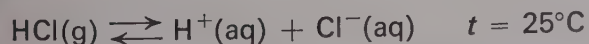
According to this idea acids could furnish H^+ in a water solution and bases could yield OH^- . Use this section to initiate three ideas:

- A "strong" electrolyte is not necessarily concentrated.
- H^+ is involved in the action of acids.
- The equilibrium expression is applicable to acids. Steps (b) and (c) will be treated further in later sections (14-4 and 14-7).

The student will, if he has any idea of acids at all, consider them as corrosive materials capable of eating through almost anything. To accept the coming sections he must use the more well-defined equilibrium expression of strength. You should instill the idea that this "strength" is not a matter of concentration (which we are not really discussing now) but one related to the tendency for ions to exist at equilibrium. For acids this means the tendency to release $H^+(aq)$. It is important for the student to realize that *hydrogen ions are all alike*. There are *not* weak and strong types of $H^+(aq)$. "Strong" merely means the acid supplies essentially all the $H^+(aq)$ it can potentially supply. "Strong" and "weak" are qualitative designations of the same information contained in K_A , referring to the extremes of very large and very small K_A .

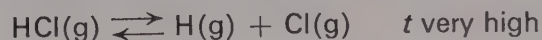
The equilibrium constant for ion formation, producing $H^+(aq)$, is related to the relative number of ions produced from a given amount of undissociated acid. A large K value means the acid gives a large fraction of ions; it is "strong." Conversely for "weak" acids. Later, in Section 14-7, the symbol K_A will make this idea quantitative and provide a ranking scale.

The nature of the important $H^+(aq)$ may come up. An exact answer is not available. Some of the difficulty can be illustrated using HCl. This gaseous compound dissolves readily in water at 25°C:



The HCl molecule is a stable one—it must be heated to a few thousand degrees before the

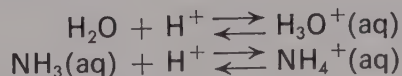
atoms will separate. Even then, neutral atoms are obtained and still higher temperatures are needed before gaseous ions are obtained.



The high temperature required to separate the two atoms of a molecule of HCl shows that HCl is very stable. Again, we can explain the solubility of HCl in water by saying $H^+(aq)$ and $Cl^-(aq)$ must also be very stable. Water must interact strongly with these ions.

This is why we have been showing such aqueous ions with the symbol (aq) to remind us that the ions interact strongly with the solvent. The symbol (aq) is purposely vague because, in most cases, chemists are not certain of the number or arrangement of the water molecules around a given ion. Many chemists suggest that the proton attaches itself strongly to one molecule of water, forming a new molecular species, $H_3O^+(aq)$, called *hydronium ion*.

Notice that the three hydrogen atoms are pictured as equivalent. There is a pleasing similarity to the formation of the well-established ammonium ion, NH_4^+ , with its four equivalent hydrogen atoms:



Still other chemists feel there are probably several arrangements of water molecules around the proton. In addition to H_3O^+ , there may be molecules such as $H_5O_2^+$, $H_7O_3^+$, $H_9O_4^+$, etc.

Unfortunately, the experimental data do not provide a definite answer to the nature of $H^+(aq)$. See the *Background Discussion*, page 283, for some details. However, the student can be given these facts. There are some water molecules clustered around the ion. These are strongly held and move with the ion—they are really part of the ion. An individual molecule of water is not indefinitely attached to one particular ion. There is some "changing of partners" caused by collisions, but the M^+ ion is constantly surrounded by water molecules. Part of the reason for the absence of a distinct result is that the $H^+(aq)$ species changes with temperature and

other conditions that affect the interaction between oxygen and the proton. This interaction is called hydrogen bonding. It was treated in Chapter 10 and will be again in 17.

14-3 The Neutralization Reaction

Expt. 31, THE HEAT OF ACID-BASE REACTIONS,

fits here. See p. 178 in the Laboratory Guide.

Demo. 32, ELECTRICAL CONDUCTIVITY OF ACIDS AND BASES,

fits here. See p. 181 in the Laboratory Guide.

Demo. 33, TITRATION,

fits here. See p. 183 in the Laboratory Guide.

14-4 The Special Roles of $H^+(aq)$ and $OH^-(aq)$

The frequently-occurring reaction of $H^+(aq)$ with $OH^-(aq)$ is used to define K_w , the ion-product of water. Bring out the similarity to the ion-product in solubility problems. K_w will be used extensively in the remainder of this chapter. The second section in this pair is to prepare the students for titration calculations. Make sure they see the "seesaw" relation. As $[H^+]$ goes up, $[OH^-]$ comes down. The product $[H^+][OH^-]$ is found to equal K_w .

A second function of these sections is to have the student understand when to ignore some source of an ion. Textbook Table 14-2, page 261, shows the technique. The background in significant figures should help here. In the first line of the Table, the values $10^{-1} M + 10^{-7} M$ appear. Written out this becomes $0.1 + 0.0000001$ which equals 0.1000001 . In this form it is easy to see that the last digit is not very important.

Expt. 32, ACID-BASE TITRATION,

fits here. See p. 184 in the Laboratory Guide.

14-5 Acid-Base Titrations

Up to this point the student has been preparing for the rest of the chapter. He has applied equilibrium concepts to the acid-base case and developed a clearer picture of hydrated ions. So far, however, he has not considered an acid and base in the same solution. This is now put before him as a series of calculations of $[H^+]$ and $[OH^-]$. The point is to dramatize the fast change near the equal molar point and to help illustrate why indicators signal the endpoint in Expt. 32.

We have treated pH rather lightly because our small use of it would not be worth the effort required to teach logarithms. If your class already has facility with logarithms, you may choose to present the pH method. Actually acidity can be expressed easily in concentration units and, indeed, that method is more straightforward. It also fits better with the equilibrium calculations the student needs to make.

14-6 The Brønsted-Lowry Definitions of Acids and Bases

This second conceptual definition is introduced for three reasons.

- It provides a broader definition and makes the acidic properties of substances such as $CO_2(aq)$ or $SO_2(aq)$ understandable.
- It confronts the student with a second set of definitions and brings him to realize there need not be a single answer to a group of facts. There are at least two more sets of definitions. See the *Background Discussion*.
- It provides the reference point in the acidity scale.

The idea of proton transfer can be compared to a series of individual strength contests. Any one of your students is strong compared to a child of 3 or 4. Any student would seem weak pitted against a professional football tackle. The proton is transferred on the basis of such "contests of strength" among various chemical compounds.

DEVELOPMENT

Make sure the student understands proton exchange and the *necessary* result that a new acid and base are produced. A less sophisticated way to say this is that if a substance has a proton and gives it away (acts as an acid), the proton can then be taken back (the new compound formed acts as a base).

The notation HB for an acid is picked to show the base contained in the acid.



As is true of any equilibrium, there are really two opposing reactions involved in this one equation,

This section also contains the important idea that *water* reacts as an *acid* or a *base*! The student may claim that water fits only one of our defining properties given in Section 14-1. It does contain hydrogen, but so do sugar, benzene, and natural gas. There are these arguments to advance: (1) In liquid water, there are some ions present; it conducts, although feebly. (2) We can detect the presence of $H^+(aq)$ and $OH^-(aq)$ ions in pure liquid water, but we cannot for the other substances named. To produce these ions, water molecules must have released protons—acted as an acid. (3) There is evidence that the proton is hydrated; that is, the water molecule must be able to accept a proton—act as a base.

14-7 The Strengths of Acids and Bases

The acid dissociation constant, K_A , is formally introduced. It follows directly from the equilibrium involved plus the inclusion in the constant of the essentially unchanging water concentration. The ability to use Table 14-4 should be cultivated. Show the student how it is a store of information to help him answer new questions. If he learns how to use it, he need not learn the answer to each specific question.

14-8 Experimental Determination of K_A

Expt. 33, DETERMINATION OF $[H^+]$ USING INDICATORS,

fits here. See p. 188 in the Laboratory Guide.

14-9 Calculation of $[H_3O^+]$

The first short section mentions the use of indicators and will be helpful in Part IVc of Experiment 33. There are no new concepts. The equilibrium ideas of Chapter 13 are applied to proton donation.

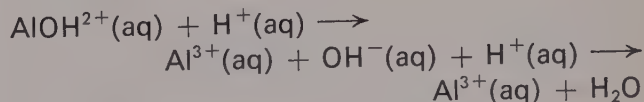
The second section gives further use of K_A . It also makes use of the idea of approximating concentration or ignoring very small contributions.

Film, ACID-BASE INDICATORS,

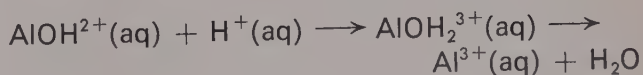
fits here. See p. 276 for Summary.

14-10 Acidic and Basic Properties of the Third Row Elements

The basic behavior of hydroxides may be treated in terms of the breaking of an $M-O$ bond or in terms of the addition of an H^+ to an $-OH$ group still attached to the metal. For example we might write



or



The two equations suggest a difference in the actual mechanism by which the process occurs. At the present our experimental methods will not differentiate the two mechanisms. Thus there is no need to make a big point of how the aquated ion is formed.

Although we can't legitimately identify differences between $Al^{3+}(aq)$ ions made by different mechanisms, we can note that a *water molecule bound to an ion such as Al^{3+} is polarized, or has a different electron configuration, and hence a different bond energy than a water molecule in the solvent.* A high positive field on the metal cation pulls electrons away from the $O-H$ bond, promoting acid behavior. On the other hand, a

weak field resulting from low charge and large size of the cation makes for a weak metal-oxygen bond, making either the loss of an OH^- or the addition of an H^+ to an attached OH^- easier. These are the extremes developed in the Text-

book. Amphoteric substances are midway between the extremes and can serve as either acid or base.

14-11 Review

Supplementary Materials

Books

C. A. VanderWerf, *ACIDS, BASES, AND THE CHEMISTRY OF THE COVALENT BOND*, Reinhold, New York (1961), pp. 11-37a.

Films

For ordering information see the *List of Film Sources* at the back of the Teacher's Guide.

ACID-BASE INDICATORS

A CHEM Study film

Running Time: 20 minutes
color

This film was made in collaboration with Dr. J. A. Campbell. It is most suitable for presentation at the conclusion of the chapter. The film summarizes certain concepts covered previously [$\text{H}^+(\text{aq})$ effects on indicators], applies some of them to new situations (equilibrium constants of indicators). A preview will help you fit the film to your needs.

Background Discussion

There are three major parts to the following discussion:

Definitions of Acids and Bases

Strengths of Acids and Bases—Ionization

Constants for Acids

The Nature of $\text{H}^+(\text{aq})$

DEFINITIONS OF ACIDS AND BASES

Have any students asked you yet, "What is the correct definition for an acid?" If not, just wait; they will. The operational concepts of acids and bases originated with the alchemists. Many of the operational criteria described in the Textbook were listed by Robert Boyle in the heyday of the phlogiston theory. Perhaps it will seem strange that a concept so old, so common, and so useful should be plagued by at least four separate sets of definitions of an acid. It is legitimate, of course, to wonder whether there is a best definition of an acid.

A number of respected chemists have referred, in their writings, to the true definition of an acid. Somewhat more introspective scientists, includ-

ing men who originated some of our current theories, have been careful to avoid such emphasis upon opinion and have placed the different systems in their proper place as *conceptual aids* used to describe experimental results. In the latter framework we can (and do) have a number of different sets of definitions of acids and bases. It seems reasonable to identify as "best" that set of definitions which interprets the pertinent experimental facts in the *simplest* and *most consistent* way. You will immediately note that this statement contains a built-in "fudge factor." The scheme which interprets the facts most simply is a matter of opinion; therefore scientists are liable to become as emotional in their views on this topic as they are in many other areas of chemistry. Most chemists agree, however, that the different systems can be arranged in order of increasing generality of application. We want to consider a number of different schemes in this light. For presentation to the students of this course, we will consider only the first two sets of definitions, the Arrhenius and the Brønsted-Lowry, since we are working primarily with water

solutions. But if we were working with non-protonic solvents or fused salts, we would find other systems, such as the Lewis theory or the solvent system, more appropriate. The selection of systems depends upon the experimental problem. Let's be dogmatic; there is no *one* correct set of definitions for either acids or bases. Various schemes are defined in subsequent sections. Different experiments are best treated in terms of whichever definition is simplest.

The Arrhenius Definitions

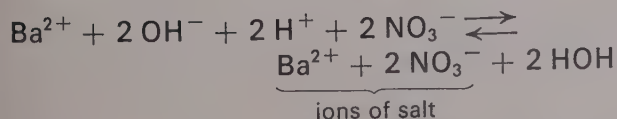
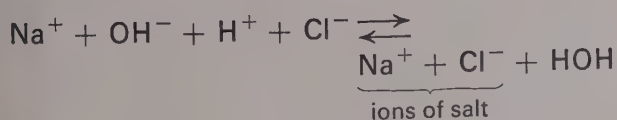
The Arrhenius definitions are applicable only in water solution; they constitute one of the oldest, most restrictive, and probably simplest, sets of definitions. They deserve emphasis because of the singular importance of the chemistry of aqueous solutions on this planet.

Acid: A chemical entity which gives hydrated hydrogen ion, $H^+(aq)$, in water solution, e.g., HCl , HSO_4^- , H_2SO_4 , HNO_3 , CH_3COOH .

Base: A chemical entity which gives hydrated hydroxide ion, $OH^-(aq)$, in water solution, e.g., $NaOH$, KOH , $Ba(OH)_2$, $[(CH_3)_4N]OH$ (tetramethylammonium hydroxide).

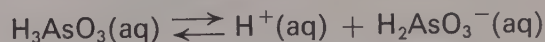
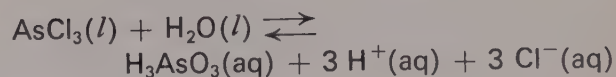
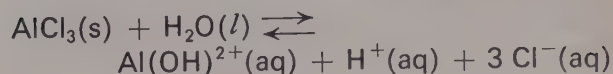
Salt: A substance, other than water, resulting from the neutralization of an acid by a base. Salts have also been defined as substances, other than compounds giving $H^+(aq)$ or $OH^-(aq)$, which crystallize in an ionic lattice, e.g., $NaCl$, K_2SO_4 , $Ba(NO_3)_2$, K_3PO_4 .

Neutralization: The reaction of an acid and a base in water to give a salt and water (*all ions aquated*):



Hydrolysis: A reaction between a compound and water in which the water molecule is

split to give $OH^-(aq)$ or $H^+(aq)$, the other ion combining with the compound.

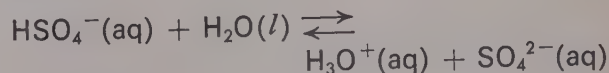
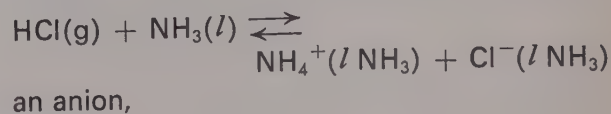


Comments: The foregoing definitions are straightforward and generally familiar to you. Except for the definition of hydrolysis, they are presented in the Textbook and will be used as a *point of reference* in considering subsequent sets of definitions. Equilibrium constants described later are applicable.

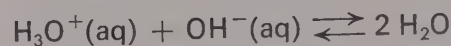
The Brønsted-Lowry Definitions

They are applicable in all solvents which can give up or accept a proton. This theory is broader than the Arrhenius theory in that it considers reactions in $NH_3(l)$, CH_3OH , CH_3COOH , and many other protonic solvents *as well as water*. Water, *the* solvent in the Arrhenius theory, is now only one of many solvents which can be used in the Brønsted-Lowry system.

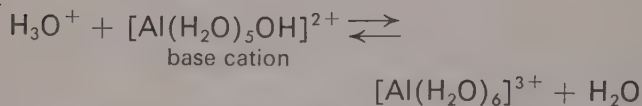
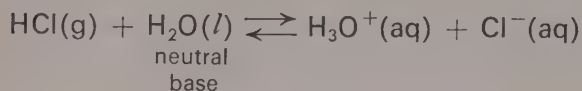
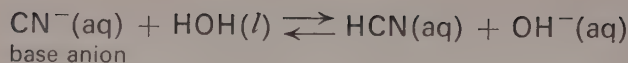
Acid: A substance which can *donate a proton* to another (acceptor) species. The acid can be a neutral molecule,



or a cation,



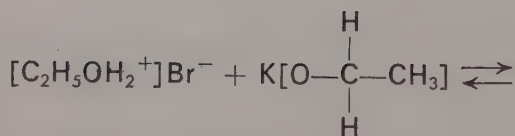
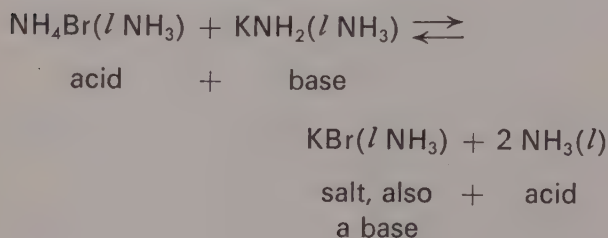
Base: A substance which can accept a proton from a Brønsted-Lowry acid. For example, the H_2O and the OH^- shown on the left in the illustrations of acids are functioning as bases. Other examples can be cited:



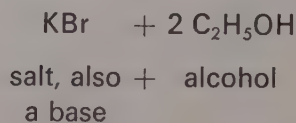
As a consequence of this set of definitions, the process of hydrolysis described separately in the Arrhenius definitions is now only another acid-base process. (See the reaction for NaCN.) You will also notice that NaOH, classed as a base in the Arrhenius theory, is now considered as a salt which contains the base OH^- . The prime difference between NaOH and NaCN in this scheme is that the base OH^- in the salt NaOH is stronger than the base CN^- in the salt NaCN. Note the greater generality of the Brønsted-Lowry scheme.

Salt: The same definition holds as in the Arrhenius scheme.

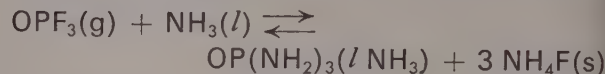
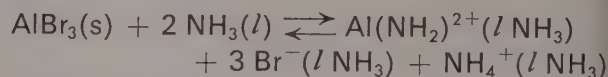
Neutralization: The same definition holds as in the Arrhenius scheme. Neutralization is the reaction of acid and base. Reactions can take place in solvents other than water, as the following equations show.



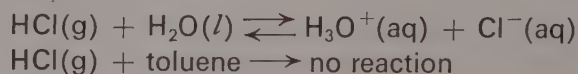
HBr in ethyl + potassium
alcohol ethoxide



Solvolysis: The specific process for breaking a water molecule can now be generalized to include solvent molecules other than water. The general term *solvolysis*, rather than the more specific *hydrolysis*, is used. For example, reactions in liquid ammonia are comparable to those in water:



Comments: Although the Brønsted-Lowry definitions are more widely applicable, the formalism becomes somewhat more restrictive, and, as a result, details of terminology become more important. You may have noticed that this set of definitions implies something about the actual mechanism of proton transfer, yet in most reactions we know nothing of the mechanism involved. We identify only initial reactants and final products, and there is even some uncertainty about the products, since we don't really know how many H_2O molecules are associated with each ion in solution. We write H_3O^+ as a matter of convenience, but there is little evidence to support this particular formula. We could write $[\text{H}(\text{H}_2\text{O})_n]^+$ as a more exact representation of the situation. The mechanistic aspect is recognized as part of our formalism. The Brønsted-Lowry concept can also be utilized outside of solution, as the reaction $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightleftharpoons \text{NH}_4\text{Cl}(\text{s})$ suggests. One of the big advantages of the Brønsted-Lowry concept is that it recognizes and emphasizes the role of the solvent in ionization processes. From experiment we know that



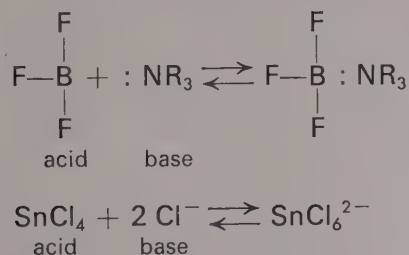
The solvent *is* important.

The Lewis Definitions

The definitions proposed by G. N. Lewis are applicable in protonic as well as nonprotonic

solvents and are equally applicable to reactions carried out in the absence of solvents. The formalism centers around the concept of the electron pair and the nebulous relation between bond type and acid-base behavior.

Acid: Any anion, cation, or neutral molecule that has an operationally incomplete electronic configuration and which can accept one or more *electron pairs* to form a coordinate bond. Among the simplest examples are these:



Base: Any anion, cation, or neutral molecule which can donate an electron pair to form a coordinate bond. You will notice that, in the two examples above, the basic trialkylamine "donates" or shares an electron pair with BF_3 to give the compound F_3BNR_3 , in which the F_3B and NR_3 are joined by a coordinate bond. Note that an ultimate grouping of eight electrons around the acid is *not* demanded in the Lewis system, since in the second example the Sn^{4+} shares *twelve* electrons with the six chloride ions surrounding it.

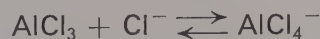
Salt: This term is not really as applicable in the Lewis system as it is in the earlier systems. If a salt must be defined, it is called an ionic solid.

Neutralization: The reaction between equivalent quantities of acid and base. The product can be a salt or any coordination compound. (The term neutralization is not really used in reference to Lewis acid-base reactions.) The reaction between copper(II) ion and ammonia to form $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is an acid-base reaction in this system.

Solvolysis: This term has no special significance in this system.

Comments: It will be noticed that the elec-

tron pair system includes all types of acid-base behavior described in all of the earlier systems. As first proposed by Lewis, the system was largely operational in character, and centered around observations of the type described. It interprets a large amount of data effectively. Confusion relative to its use may arise when attempts to interpret electron distribution and bond type are superimposed upon Lewis' original operational definition. For example, some people have noted that an electron pair may not really bind Cl^- to AlCl_3 in the complex AlCl_4^- , but the binding may be an electrostatic attraction between one Al^{3+} ion and four Cl^- ions. If this is true, then the process



falls outside the strict Lewis definition of acid-base processes, since we can't identify a shared electron pair. Such problems, of course, are man-made and are not inherent in the *operational* application of the system. But the concepts of acid-base behavior *are* operational in character, and difficulties arise when we try to impose strict interpretations of electron distribution upon the definitions. Unfortunately, the pertinent data that would allow proper consideration of the questions raised are usually unavailable.

The Solvent System Definitions

The solvent system definitions are applicable in protonic as well as nonprotonic solvents. The primary emphasis is upon the solvent used, not upon the proton transfer.

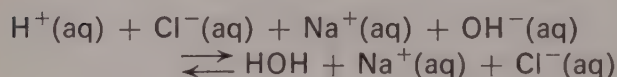
Acid: Any cation, anion, or neutral molecule giving a *cation that is characteristic of the solvent*. In water, H^+ is the characteristic cation of the solvent, since water is assumed to ionize according to the equilibrium $\text{HOH} \rightleftharpoons \text{H}^+ + \text{OH}^-$. In liquid NH_3 , the cation that characterizes the solvent is again H^+ , since NH_3 is assumed to ionize according to the process $\text{NH}_3 \rightleftharpoons \text{H}^+ + \text{NH}_2^-$. In the non-protonic solvent nitrosyl chloride, NOCl , the cation NO^+ is characteristic of the solvent, since the formal process $\text{NOCl} \rightleftharpoons \text{NO}^+ + \text{Cl}^-$ is assumed.

Base: Any cation, anion, or neutral molecule giving an *anion that is characteristic of the solvent*. The equations for the ionization processes in HOH, NH₃, and NOCl indicate that compounds containing ionizable or reactive OH⁻, NH₂⁻, and Cl⁻ will each be bases in the respective solvents HOH, NH₃, and NOCl.

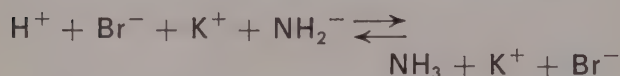
Salt: As before, a salt is defined as an ionic solid.

Neutralization: Again, this is a process involving chemical interaction of equivalent quantities of acid and base to give a salt and one mole of the solvent.

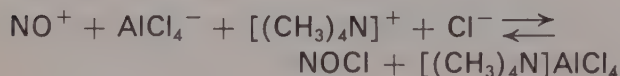
In water:



In liquid NH₃ (each species is in liquid NH₃):

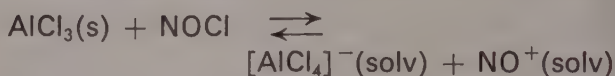
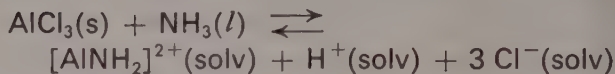
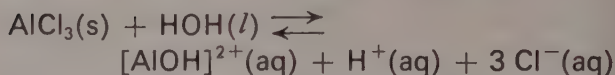


In liquid NOCl (each species is in liquid NOCl):



Solvolysis: The specific processes for protonic molecules such as H₂O and NH₃ can now be generalized to include nonprotonic solvents. Solvolysis now implies any process which promotes breaking the solvent molecule into its ions, one of which is usually tied up chem-

ically. Compare the following examples.



In each reaction the cation that characterizes the solvent is generated as a result of a process which formally appears to break the solvent molecule into a positive and a negative ion.

Comments: You will recognize that this system resembles the Brønsted-Lowry system but is broadened to apply to many solvents, not just water. We also achieve an increase in the formalism of the system. We now have to assume ionization of our solvents according to set patterns, and we must assume ionic mechanisms even though such an assumption may be unproved or highly doubtful. Note that all examples considered in the Arrhenius and Brønsted-Lowry systems are automatically included in the Solvent system definitions. As a means of correlating information and predicting products from reactions, this scheme has much to recommend it, but we must be careful in accepting a literal interpretation of the description of the processes considered.

Summary of Acid-Base Systems

We can summarize what has been stated in the foregoing as follows:

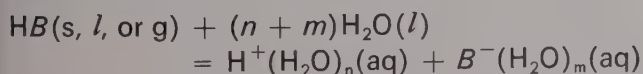
	Acid	Base	Formation of Acid or Base
Arrhenius	contains H ⁺	contains OH ⁻	Ionization in water.
Brønsted-Lowry	donates H ⁺	accepts H ⁺	Donation in water.
Lewis	accepts an electron pair	donates an electron pair	Acid and base molecules come together. Can be in any solvent, but none required.
Solvent-system	gives a solvent cation	gives a solvent anion	Donation in solvent.

The first three are progressively more general. The first specifies the composition of acids, bases, and solvents; the second stipulates the solvent and, in part, the acid composition; the third implies something about acids (electron-accepting capacity) and bases (donating capacity).

STRENGTHS OF ACIDS AND BASES—IONIZATION CONSTANTS FOR ACIDS

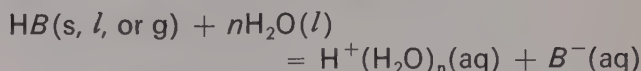
The Textbook covers K_A for simple ionization theory of acids. The following paragraphs develop the corresponding relation for the Brønsted-Lowry view. Such material is not needed in most classes but will be helpful for interested students. The problem of the "concentration of water," dealt with very briefly in the Textbook, receives additional treatment here.

What determines the strength of an acid? Since we can't agree as to what an acid is, it should not be surprising to find that we are even more uncertain about acid strength when considered in general terms. One thing is abundantly clear, *the concept of acid strength can be defined only in terms of some rather arbitrarily selected experimental parameters*. Parameters appropriate to all systems of acids and bases have not been found, but if we restrict our interest to aqueous solutions of acids and bases, the situation becomes more encouraging. For purposes of discussion let us select a modification of the Brønsted-Lowry scheme and discuss the general acid HB in water, where B^- is any anion. The appropriate equation is then



Both ions, H^+ and B^- , owe their stability in aqueous solution to a strong interaction with the solvent, called aquation. In the equation, we show explicitly the H_2O molecules in the first hydration sphere, these being considered to be bound much more strongly than any others. Both for $H^+(H_2O)_n$ and $B^-(H_2O)_m$, the values of n and m are unknown. We shall investigate the effect on the equilibrium expression to include,

specifically, the hydration. We shall concentrate on $H^+(H_2O)_n(aq)$ —since our interest is in acids at this point—by suppressing in the equation the hydration of $B^-(aq)$, even though there is no experimental evidence that the aquation of B^- (or other anions and cations) is less important than that of H^+ . Hence we write



Since we can't be sure how many water molecules will be associated with each proton, we have indicated our uncertainty by writing n as the number of water molecules involved. As you will see, the number of water molecules is unimportant, but it *is* important to recognize that *water serves as the reference base in all cases*. We are comparing all acids by using a standard base. This simplifies our comparison tremendously. Another simplifying assumption lies in our decision to use the ionization process in the solvent water as a measure of acid strength. If we are willing to accept the aforementioned limitations, the problem of relative acid strength is subject to direct experimental attack. The concentration of cation and anion can be determined from measurements of conductivity, and the concentration of nonionized HB can be determined from stoichiometry. The concentration relationships at equilibrium can be expressed directly by the equilibrium constant for our defining equation:

$$K' = \frac{[H^+(H_2O)_n][B^-]}{[H_2O]^n[HB]}$$

We note in the above relationship the quantity $[H_2O]^n$; it is the only quantity not specifically mentioned in our discussion of measurement. What is the concentration of water in an aqueous solution? What is the value of n ? Let's consider the second question first. The absolute value of n escapes us at the present time ($n = 4$ seems to have stronger support than $n = 1$), but we feel safe in assuming that n is the same for the proton, regardless of its source. That is, *the number of water molecules around an H^+ ion will be the same whether the proton comes from HCl , H_2SO_4 ,*

or HNO_3 , etc., in water solution. Let's look at the first question now. The laws of stoichiometry will permit us to estimate the "concentration" of water in various solutions in terms of number of moles of water per liter of solution. Several representative calculations are summarized in Table I. Examine carefully the columns set in boldface type in Table 11-I. You will note that the "concentration" of water in all solutions is relatively constant and changes only about 3.5%

as we go from pure water to 1.0 M H_2SO_4 . In more dilute solutions, changes are trivial. As a simplification, let us neglect these small changes in the concentration of water and write

$$K' = \frac{[\text{H}^+(\text{H}_2\text{O})_n][\text{B}^-]}{[\text{H}_2\text{O}]^n[\text{HB}]} = \frac{[\text{H}^+(\text{H}_2\text{O})_n][\text{B}^-]}{C^n[\text{HB}]}$$

where C is now the concentration of water and is assumed to be constant at about 55.5* moles/liter.

TABLE 11-I
Concentration of Water in Some Common Acidic and Basic Solutions

Acid Solution	Density (g/liter)	Acid Present (g/liter)	H_2O (g/liter)	H_2O (moles/liter)	Base Solution	Density (g/liter)	Base Present (g/liter)	H_2O (g/liter)	H_2O (moles/liter)
Pure H_2O	1000	0	1000	55.5	Pure H_2O	1000	0	1000	55.5
0.1 M HCl	1001	3.6	997	55.5	0.1 M NaOH	1004	4	1000	55.5
0.1 M H_2SO_4	1005	9.8	995	55.4	0.1 M $\text{Ba}(\text{OH})_2$	1015	17	998	55.5
0.5 M HCl	1008	18.0	990	55.0	0.5 M NaOH	1021	20	1001	55.5
0.5 M H_2SO_4	1032	48.0	984	54.6	0.5 M $\text{Ba}(\text{OH})_2$	—	—	—	—
1.0 M HCl	1018	36.5	981	54.5	1.0 M NaOH	1042	40	1002	55.6
1.0 M H_2SO_4	1061	96.0	965	53.6	1.0 M $\text{Ba}(\text{OH})_2$	—	—	—	—

We can simplify the previous equation.

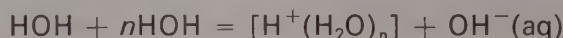
$$K' \times C^n = \frac{[\text{H}^+(\text{H}_2\text{O})_n][\text{B}^-]}{[\text{HB}]} = K_A = \frac{[\text{H}^+(\text{aq})][\text{B}^-]}{[\text{HB}]}$$

We find that, for an acid, the term for the water concentration is included as part of the ionization constant. For this reason, it is important to note that we haven't overlooked the concentration of water in writing our equilibrium constant but have included the constant value C^n in our value of K_A .

Our values of K_A then give a quantitative estimate of the strength of an acid. A large value of K_A indicates a *strong* acid; a small value of K_A indicates a *weak* acid. (Remember that 10^4 is *larger* than 10^2 , but 10^{-4} is *smaller* than 10^{-2} .) Acids can then be arranged in order of decreasing acid strength as shown in the Textbook (p. 267).

The special case of water as an acid is interesting because it provides the foundation for one

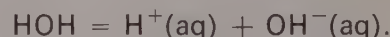
scale for reporting $[\text{H}^+]$ in water solution—the pH scale. *Water is an acid.* Let us examine the implications of this statement. If water is an acid it should undergo some ionization to yield H^+ and OH^- in accordance with the equation



or



The earlier arguments given for the general acid HB indicate that we can safely write



The equilibrium constant is

$$K' \times C^n = K_A = \frac{[\text{H}^+][\text{OH}^-]}{[\text{HOH}]} = \frac{[\text{H}^+][\text{OH}^-]}{C}$$

* Because of uncertainties in the "activity" of water in aqueous solutions, we don't know the exact value of C^n , but this is unimportant as long as it is reasonably constant. The constant K_A is the measurable quantity, and because of variations in activity of both positive and negative ions, as well as HB and water, K_A shows a gradual variation as the concentration of the solution changes.

Thus

$$K' \times C^n \times C = K_A \times C = [H^+][OH^-] = K_w$$

which is the expression given in the Textbook at the bottom of p. 259. Note that K_A differs from K_w by the factor C .

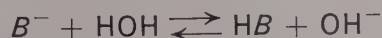
In discussing the pH scale and the conversion of $[H^+]$ values to pH , a review of logarithms and the material on exponents in Appendix 6 of the Laboratory Manual will be helpful. A typical problem might ask: What is the $[H^+]$ value for a solution of $pH = 5$? From the definition of pH we know that a solution of $pH = 5$ has an $[H^+]$ of 10^{-5} . A related question is: What is the $[H^+]$ for a solution of $pH = 4.75$? We know by inspection that the value will be close to that for the solution of $pH = 5$, so this will immediately serve as a rough check on our answer. The $[H^+] = 10^{-4.75}$ by definition of pH . Since we add exponents in multiplying, we can write

$$10^{-4.75} = 10^{0.25} \times 10^{-5.00}$$

or

$$[H^+] = 1.8 \times 10^{-5}$$

If we use the Brønsted-Lowry definition of a base, we must again select a common acid and a standard solvent for comparison of base strengths. If we take advantage of the fact that water can either lose or gain a proton, we can then use water as a standard acid, much as we used it as a standard base in our study of acids. The key equation becomes



(You will note that this is simply the hydrolysis equation for the ion B^- in terms of the Arrhenius definitions.) If the above equation proceeds to the right rather strongly, B^- is a strong base; if the reaction doesn't proceed to any measurable extent, B^- is a weak base. The equilibrium constant will again be useful.

Writing the equilibrium expression

$$K' = \frac{[HB][OH^-]}{[B^-][HOH]}$$

we can take advantage of our relatively constant value of $[HOH]$, giving

$$K'[\text{HOH}] = K' \times C = \frac{[HB][OH^-]}{[B^-]} = K_{\text{hyd}} \text{ or } K_B$$

We next substitute the relation

$$[OH^-] = \frac{10^{-14}}{[H^+]}$$

from the relation $[H^+][OH^-] = 10^{-14}$ and we get

$$K_B = \frac{[HB] 10^{-14}}{[B^-][H^+]} = \frac{10^{-14}}{K_A}$$

Again, a large value of K_B indicates a strong base, and a small value indicates a weak base.

THE NATURE OF $H^+(aq)$

Because of the great practical importance of aqueous acid solutions, a vast amount of study has been devoted to the identification of the important species in them. The question has come down to clarification of the structure represented by $H^+(aq)$. There is great appeal to the proposal that the species is a unique one *and* that it is H_3O^+ . One of the big advantages in using H_3O^+ is pedagogic, but it would not be fair to use this symbolism so exclusively and consistently that the student is left with a strong impression that the issue is settled beyond doubt. In fact, in view of the considerable doubt that does remain, your discussion of $H^+(aq)$ presents a desirable opportunity to stress the many important chemical problems that remain unsolved.

A wide variety of suitable methods exists for the identification of molecular species. A list of these follows, with brief comments on their application to the $H^+(aq)$ problem. References (indicated by number) are given at the end.

Nuclear Magnetic Resonance

Two research groups (1, 2) have made NMR studies of strong acid solutions. They interpret their data in terms of H_3O^+ but do not allow for hydrogen bonding, an effect expected to be as large as the effects attributed to H_3O^+ .

Solid $HClO_4 \cdot H_2O$ gives a NMR pattern which has been reported (3) to show H_3O^+ in the crystal. Aside from our preference for knowing

the structure in solution rather than in a solid, the data yield only average interproton distances around a central oxygen atom.

Infrared

The paper based on this technique (4) has been criticized (5) because some solutions were so concentrated there was a shortage of H_2O to form such species as H_9O_4^+ and H_3O^+ , and in the less concentrated samples the bands attributed to H_3O^+ were absent.

Mass Spectroscopy

Acid solutions have been vaporized and the gas shown to contain relatively large amounts of H_9O_4^+ and H_3O^+ , with smaller amounts of H_5O_2^+ and H_7O_3^+ . Thus the hydrated species are shown to exist in the gaseous state.

Relaxation Methods

Data from sound adsorption, dielectric dispersion, and similar measurements have been reviewed (4) with the conclusion that H_9O_4^+ is the predominant species in solution (if sufficient water is present). It is not clear whether there is a pyramidal or tetrahedral arrangement of four water molecules.

This résumé indicates that the existence of H_3O^+ as the unique and predominant species in aqueous acids cannot be considered more than a working hypothesis. The 1958 review (5) concludes that the best evidence is for H_9O_4^+ , but it is not unique.

REFERENCES

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2. G. C. Hood, O. Redlich, and C. A. Reilly, Ionization of strong electrolytes III. Proton magnetic resonance in nitric, perchloric, and hydrochloric acids, *J. Chem. Phys.*, **22**, 2067 (1954).
3. J. A. S. Smith and R. E. Richards, Nuclear magnetic resonance spectra of some inorganic hydrates, *Trans. Faraday Soc.*, **48**, 307, 675 (1952).
4. M. Falk and P. A. Giguère, Infrared spectrum of the H_3O^+ ion in aqueous solutions, *Can. J. Chem.*, **35**, 1195 (1957).
5. M. Eigen and L. De Maeyer, Self-dissociation and protonic charge transport in water and ice, *Proc. Roy. Soc. (London)*, **247**, 505 (1958).

Answers to Exercises and Problems

Exercise 14-1

Show that the concentration of H_2O in a liter of pure water is 55.5 *M*. Assume that the mass of one liter of water is 1.00×10^3 grams.

Answer

$$\frac{1.00 \times 10^3 \text{ g/liter}}{18 \text{ g/mole}} = 55.5 \text{ moles/liter} = 55.5 \text{ } M$$

Exercise 14-2

What is the concentration of H_2O in 1.00×10^2 ml of water? in 1.00 ml?

Answer

The concentration of any given liquid or solution is the same for any amount. Mathematically, the proof is simple.

$$\begin{aligned} \text{For 100 ml} \quad & \frac{100 \times 10^2 \text{ ml} \times 1 \text{ g/ml}}{18 \text{ g/mole}} \\ &= 5.55 \text{ moles/100 ml or } 55.5 \text{ moles/liter} \\ \text{For 1 ml} \quad & \frac{1 \text{ ml} \quad 1 \text{ g/ml}}{18 \text{ g/mole}} \\ &= 0.0555 \text{ mole/ml or } 55.5 \text{ moles/liter} \end{aligned}$$

Exercise 14-3

Show that the addition of 0.010 mole of solid NaOH to 1.0 liter of water reduces the concentration of $H^+(aq)$ to $1.0 \times 10^{-12} M$.

Answer

$$[OH^-] = 0.010 \text{ mole/liter} = 1.0 \times 10^{-2} M$$

$$[H^+] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12} M$$

Exercise 14-4

Suppose that 3.65 grams of HCl are dissolved in 10.0 liters of water. What is the value of $[H^+]$? Show that $[OH^-] = 1.00 \times 10^{-12} M$.

Answer

$$[H^+] = \frac{3.65 \text{ g HCl}}{36.5 \text{ g HCl/mole} \times 10.0 \text{ liters}}$$

$$= 0.100 \text{ mole HCl/10.0 liters}$$

$$= 1.00 \times 10^{-2} M$$

$$[OH^-] = \frac{1.00 \times 10^{-14}}{1.00 \times 10^{-2}} = 1.00 \times 10^{-12} M$$

Exercise 14-5

How many hydrogen and hydroxide ions would there be in 1 liter of H_2O ?

How many hydrogen and hydroxide ions would there be in 1 liter of 0.1 M HCl?

Answer

$$[H^+] = [OH^-] = 1.0 \times 10^{-7} M$$

$$1.0 \times 10^{-7} \times 6.0 \times 10^{23}$$

$$= 6.0 \times 10^{16} H^+ \text{ or } OH^- \text{ ions per liter of pure water}$$

In 0.1 M HCl

$$H^+ = 1 \times 10^{-1} \times 6.0 \times 10^{23} = 6.0 \times 10^{22} \text{ ions/liter}$$

$$OH^- = 1 \times 10^{-13} \times 6.0 \times 10^{23} = 6.0 \times 10^{10} \text{ ions/liter}$$

Exercise 14-6

Calculate the $[H^+]$ and $[OH^-]$ for the titration just discussed when 0.0999 mole of NaOH(s) has been added.

Answer

$$[H^+] = 0.1 - 0.0999 \text{ or } 1 \times 10^{-4} M$$

$$[OH^-] = \frac{1 \times 10^{-14}}{1 \times 10^{-4}} = 1 \times 10^{-10} M$$

Exercise 14-7

You have 100 ml of an HCl solution whose concentration you do not know. Titration with 0.10 M NaOH solution requires 50 ml of the base to reach the equivalence point. What was the original concentration of the HCl solution?

Answer

$$\text{moles } OH^- \text{ used} = \text{moles } H^+ \text{ present}$$

$$(0.10 \text{ mole/liter}) \left(\frac{1 \text{ liter}}{1000 \text{ ml}} \right) (50 \text{ ml}) = \text{moles } OH^- \text{ used} = 0.005$$

$$\text{moles } H^+ / 100 \text{ ml} = 0.005$$

$$\text{moles } H^+ / \text{ml} = 0.00005$$

$$\text{moles } H^+ / \text{liter} = 0.05$$

$$[H^+] = 0.05 M$$

Exercise 14-8

Which of the following acids is the strongest and which is the weakest? Use Appendix 3 to verify your answer.

nitrous acid	HNO_2	$K_A = 5.1 \times 10^{-4}$
sulfurous acid	H_2SO_3	$K_A = 1.7 \times 10^{-2}$
phosphoric acid	H_3PO_4	$K_A = 7.1 \times 10^{-3}$

Answer

H_2SO_3 is the strongest; its K_A is largest.

HNO_2 is the weakest; its K_A is smallest.

Exercise 14-9

Convince yourself that the equilibrium constant for the reaction



is $1/K_A$ where K_A is the equilibrium constant for the reaction



Answer

Taking the second equation,

$$K_A = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]}$$

For the first equation the equilibrium constant is equal to

$$\frac{[\text{HCO}_3^-]}{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}$$

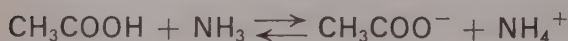
Clearly this is $1/K_A$.

Exercise 14-10

Are reactants or products favored in the reaction between CH_3COOH and NH_3 ? Use the qualitative guide just discussed to answer this question.

Answer

A possible reaction is



The acid CH_3COOH is above the base NH_3 in Table 14-4; so the reaction, hence products, will be favored.

Problem 1

Vinegar, lemon juice, and curdled milk, all taste sour. What other properties would you expect them to have in common?

Answer

- (i) They should contain hydrogen-containing compounds.
- (ii) Their aqueous solutions should conduct electricity.
- (iii) Their aqueous solutions should liberate hydrogen gas when zinc metal is put in them.
- (iv) Their aqueous solutions should turn litmus red.

Problem 2

Give the name and formula of three hydrogen-containing compounds that are not classified as acids. State for each compound one or more properties common to acids that it does not possess.

Answer

Among the possible answers are:

Hydrogen gas, H_2	Aqueous solutions do not conduct.
Sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$	Lacks sourness; solutions do not conduct.
Methane, CH_4	In contact with zinc, it does not release hydrogen gas.

Sodium hydroxide, NaOH Lacks sourness.

Problem 3

Devise an operational and also a conceptual definition of a gas.

Answer

Operational definition: Gases are easily compressed, have low density, and diffuse until they uniformly fill a container. The definition can include other observed properties.

Conceptual definition: Gases consist of molecular particles which possess very little attraction for each other.

Problem 4

At 20°C , 0.009 g of $\text{Mg}(\text{OH})_2$ will dissolve to make a liter of saturated solution. The magnesium hydroxide that dissolves also ionizes. Is $\text{Mg}(\text{OH})_2$ a strong or weak electrolyte? Determine $[\text{OH}^-]$.

Answer

$\text{Mg}(\text{OH})_2$ is a strong electrolyte since all "that dissolves also ionizes." See Textbook, p. 257, just under Table 14-1 where 100% ionization is given as the criterion of a strong electrolyte.

$$0.009 \text{ g } \text{Mg}(\text{OH})_2 = \frac{0.009 \text{ g}}{58 \text{ g/mole}} = 0.00016 \text{ mole}$$



$$[\text{Mg}^{2+}] = 1.6 \times 10^{-4} M$$

$$[\text{OH}^-] = 2(1.6 \times 10^{-4}) \text{ or } 3.2 \times 10^{-4} M$$

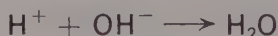
Problem 5

What will happen to the equilibrium



as OH^- ions are added? Even though CH_3COOH is a weak acid, one mole of it will require how many moles of OH^- for neutralization?

Answer



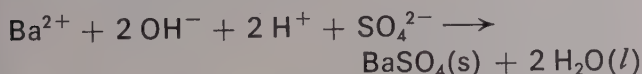
That will cause more acetic acid to ionize and a new equilibrium condition to be established. One mole of acid will require one mole of OH^- for neutralization.

Problem 6

As a solution of barium hydroxide is mixed with a solution of sulfuric acid, a white precipitate forms and the electrical conductivity decreases markedly. Write equations for the reactions that occur and account for the conductivity change.

Answer

BaSO₄(s) precipitates, and H₂O forms. Both reactions reduce the number of ions. The electrical conductivity drops because there are fewer ions to carry the current.



Note: This question is based on Demonstration 32; see Laboratory Guide p. 181.

Problem 7

What is the concentration of H⁺(aq) in an aqueous solution in which [OH⁻] = 1.0 × 10⁻³ M?

Answer

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{1.00 \times 10^{-3}} = 1.00 \times 10^{-11} \text{ M}$$

Problem 8

The 100 ml of the HCl solution described in Exercise 14-7 (page 264) is diluted with water to 1.00 liter. What is the concentration of H⁺(aq)? What is [OH⁻] in this solution?

Answer

The HCl solution in Ex. 14-7 is 0.0100 M. The dilution reduces [H⁺] to 0.00100 M, or 1.00 × 10⁻³ M.

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.00 \times 10^{-14}}{1.00 \times 10^{-3}} = 1.00 \times 10^{-11}$$

Problem 9

An eyedropper is calibrated by counting the number of drops required to deliver 1.0 ml. Twenty drops are required.

- What is the volume of one drop?
- Suppose one such drop of 0.20 M HCl is added to 100 ml of water. What is [H⁺]?
- By what factor did [H⁺] change when the one drop was added?

Answer: (c) [H⁺] increased 1000-fold.

Answer

- Since twenty drops = 1.0 ml,

$$1 \text{ drop} = \frac{1.0}{20} = 0.050 \text{ ml (average)}$$

$$\begin{aligned} \text{(b)} \quad 0.050 \text{ ml} &= 5.0 \times 10^{-2} \text{ ml} \\ &= 5.0 \times 10^{-5} \text{ liter} \end{aligned}$$

$$\begin{aligned} (5.0 \times 10^{-5} \text{ liter}) \left(0.20 \frac{\text{mole}}{\text{liter}} \right) \\ = 1.0 \times 10^{-5} \text{ mole HCl} \end{aligned}$$

$$[\text{H}^+] = \frac{1.0 \times 10^{-5} \text{ mole}}{0.100 \text{ liter}} = 1.0 \times 10^{-4} \text{ M}$$

- [H⁺] changed from 1.0 × 10⁻⁷ M to 1.0 × 10⁻⁴ M. The factor of change is

$$\frac{1.0 \times 10^{-4}}{1.0 \times 10^{-7}} = 1000$$

Problem 10

Suppose drops of 0.10 M NaOH are added, one at a time, to 100 ml of 0.20 M HCl. See Problem 9 for description of the dropper.

- What will be [H⁺] after one drop is added?
- What will be [H⁺] after two drops are added?
- What will be [H⁺] after three drops are added?

Answer

The solution initially contains 1.0 × 10⁻⁵ mole of HCl, and as base is added, the reaction H⁺(aq) + OH⁻(aq) → H₂O occurs. Each drop of base solution adds 0.050 ml, or 5.0 × 10⁻⁵ liter, of solution, or

$$\begin{aligned} (5.0 \times 10^{-5}) \left(0.10 \frac{\text{mole}}{\text{liter}} \right) \\ = 5.0 \times 10^{-6} \text{ mole NaOH} \end{aligned}$$

- After one drop of NaOH is added, the solution contains an excess of H⁺(aq), found to be 1.0 × 10⁻⁵ mole HCl - 0.50 × 10⁻⁵ mole NaOH. Reaction consumes most of the OH⁻ added, leaving the excess 0.50 × 10⁻⁵ moles H⁺(aq) in the 100 ml.

$$[\text{H}^+] = \frac{0.50 \times 10^{-5} \text{ mole}}{0.100 \text{ liter}} = 5.0 \times 10^{-5} \text{ M}$$

- After two drops of NaOH are added, there is excess of neither H⁺(aq) nor OH⁻(aq).

Since $[H^+] = [OH^-]$, we then have

$$[H^+] = \sqrt{K_w} = 1.0 \times 10^{-7} M$$

- (c) With three drops of NaOH solution, there is an excess of $OH^-(aq)$, since 1.5×10^{-5} mole NaOH was added to the original 1.0×10^{-5} mole HCl. The excess, 0.5×10^{-5} mole $OH^-(aq)$, is present in 100 ml, thus the hydroxide ion concentration is

$$[OH^-] = \frac{0.5 \times 10^{-5}}{0.100} = 5 \times 10^{-5} M$$

Hence

$$[H^+] = \frac{1.0 \times 10^{-14}}{5 \times 10^{-5}} = 2 \times 10^{-10} M$$

Problem 11

Calculate $[H^+]$ and $[OH^-]$ in a solution made by mixing 50.0 ml 0.200 M HCl and 49.0 ml 0.200 M NaOH.

Answer: $[OH^-] = 5 \times 10^{-12} M$.

Answer

$$\begin{aligned} \text{Moles HCl} &= \left(\frac{50.0}{1000} \text{ liter} \right) \times \left(0.200 \frac{\text{mole}}{\text{liter}} \right) \\ &= 1.00 \times 10^{-2} \end{aligned}$$

$$\begin{aligned} \text{Moles NaOH} &= \left(\frac{49.0}{1000} \text{ liter} \right) \times \left(0.200 \frac{\text{mole}}{\text{liter}} \right) \\ &= 0.980 \times 10^{-2} \end{aligned}$$

Excess

$$\begin{aligned} \text{moles HCl} &= (1.00 \times 10^{-2} - 0.98 \times 10^{-2}) \\ &= 0.02 \times 10^{-2} \end{aligned}$$

$$[H^+] = \frac{0.02 \times 10^{-2}}{0.099} = 0.002 M$$

$$[OH^-] = \frac{1.00 \times 10^{-14}}{0.002} = 5 \times 10^{-12} M$$

Problem 12

Calculate $[H^+]$ and $[OH^-]$ in a solution made by mixing 50.0 ml 0.200 M HCl and 49.9 ml 0.200 M NaOH.

Answer

$$\begin{aligned} \text{Moles HCl} &= \left(\frac{50.0}{1000} \text{ liter} \right) \times \left(0.200 \frac{\text{mole}}{\text{liter}} \right) \\ &= 1.00 \times 10^{-2} \end{aligned}$$

$$\begin{aligned} \text{Moles NaOH} &= \left(\frac{49.9}{1000} \text{ liter} \right) \times \left(0.200 \frac{\text{mole}}{\text{liter}} \right) \\ &= 0.998 \times 10^{-2} \end{aligned}$$

Excess

$$\begin{aligned} \text{moles HCl} &= (1.00 \times 10^{-2} - 0.998 \times 10^{-2}) \\ &= 0.002 \times 10^{-2} \end{aligned}$$

$$[H^+] = \frac{2 \times 10^{-5}}{0.0999} = 2 \times 10^{-4} M$$

$$[OH^-] = \frac{1.00 \times 10^{-14}}{2 \times 10^{-4}} = 5 \times 10^{-11} M$$

Problem 13

How much more 0.200 M NaOH solution must be added to the solution in Problem 12 to change $[H^+]$ to $10^{-7} M$?

Answer

Enough to make the number of moles of HCl and NaOH exactly equal. This is $50.0 - 49.9 = 0.1$ ml NaOH.

Problem 14

If the pH of a solution is 5, what is $[H^+]$? Is the solution acidic or basic?

Answer

Since $pH = -\log [H^+]$ and $pH = 5$, then

$$[H^+] = 10^{-5} \frac{\text{mole}}{\text{liter}}$$

The solution is acidic, since 10^{-5} is greater than $10^{-7} M$.

Problem 15

What is $[H^+]$ in a solution of $pH = 8$? Is the solution acidic or basic? What is $[OH^-]$ in the same solution?

Answer

Since $pH = -\log [H^+]$ and $pH = 8$, then

$$[H^+] = 10^{-8} \frac{\text{mole}}{\text{liter}}$$

The solution is basic, since $[H^+]$ is less than $10^{-7} M$.

Since, at $25^\circ C$,

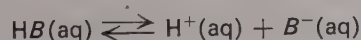
$$[H^+][OH^-] = 10^{-14}$$

then

$$[\text{OH}^-] = \frac{10^{-14}}{[\text{H}^+]} = \frac{10^{-14}}{10^{-8}} = 10^{-6} M$$

Problem 16

An acid is a substance HB that can form $\text{H}^+(\text{aq})$ in the equilibrium:



- Does equilibrium favor reactants or products for a strong acid?
- Does equilibrium favor reactants or products for a very weak acid?
- If acid HB_1 is a stronger acid than acid HB_2 , is K_1 a larger or smaller number than K_2 ?

$$K_1 = \frac{[\text{H}^+][\text{B}_1^-]}{[\text{HB}_1]} \quad K_2 = \frac{[\text{H}^+][\text{B}_2^-]}{[\text{HB}_2]}$$

Answer

- Products.
- Reactants.
- K_1 is a larger number than K_2 .

Problem 17

- Which of the following acids is the strongest and which is the weakest?
ammonium ion, NH_4^+ (in an NH_4Cl solution);
hydrogen sulfate ion, HSO_4^- (in a KHSO_4 solution);
hydrogen sulfide, H_2S .
- If 0.1 M solutions are made of NH_4Cl , KHSO_4 , and H_2S , in which will $[\text{H}^+]$ be highest and in which will it be lowest?

Answer

- From Textbook Appendix 3, we find

$$K_{\text{HSO}_4^-} = 1.3 \times 10^{-2} \quad (\text{strongest of the three});$$

$$K_{\text{H}_2\text{S}} = 1.0 \times 10^{-7};$$

$$K_{\text{NH}_4^+} = 5.7 \times 10^{-10}$$

(weakest of the three).

- $[\text{H}^+]$ is largest in the HSO_4^- solution.
 $[\text{H}^+]$ is smallest in the NH_4^+ solution.

Problem 18

From a study of Appendix 3, what generalization can you make concerning acids which contain more than one atom of hydrogen in their molecules or ions?

Answer

The acid donating the first proton is much

stronger than the second, which is in turn stronger than the third. Pauling quotes about 10^5 for the ratio of succeeding steps; i.e.,

$$\frac{K_A (1\text{st H})}{K_A (2\text{nd H})} \text{ is about } 10^5$$

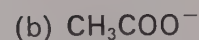
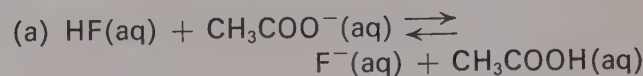
$$\frac{K_A (2\text{nd H})}{K_A (3\text{rd H})} \text{ is about } 10^5$$

Problem 19

When sodium acetate, CH_3COONa , is added to an aqueous solution of hydrogen fluoride, HF , a reaction occurs in which the weak acid HF loses H^+ .

- Write the equation for the reaction.
- What base is competing with F^- for H^+ ?

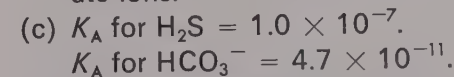
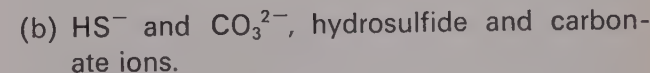
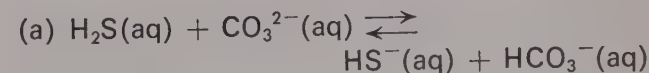
Answer



Problem 20

- Write the equation for the reaction that shows the acid-base reaction between hydrogen sulfide, H_2S , and carbonate ion, CO_3^{2-} .
- What are the two bases competing for H^+ ?
- From the values of K_A for these two acids, predict whether the equilibrium favors reactants or products.
Answer: (c) Products.

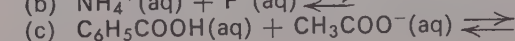
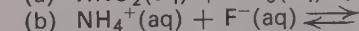
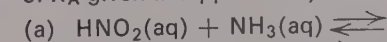
Answer



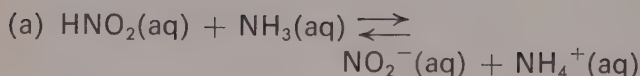
Since H_2S releases H^+ much more readily than does HCO_3^- , the reaction favors products, $\text{HS}^-(\text{aq})$ and $\text{HCO}_3^-(\text{aq})$.

Problem 21

Write the equations for the reaction between each of the following acid-base pairs. For each reaction, predict whether reactants or products are favored (using values of K_A given in Appendix 3).



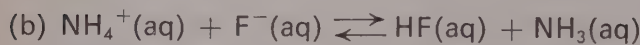
Answer



$$K_A(\text{HNO}_2) = 5.1 \times 10^{-4}$$

$$K_A(\text{NH}_4^+) = 5.7 \times 10^{-10}$$

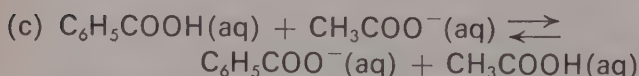
Products favored.



$$K_A(\text{NH}_4^+) = 5.7 \times 10^{-10}$$

$$K_A(\text{HF}) = 6.7 \times 10^{-4}$$

Reactants favored.



$$K_A(\text{C}_6\text{H}_5\text{COOH}) = 6.6 \times 10^{-5}$$

$$K_A(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$$

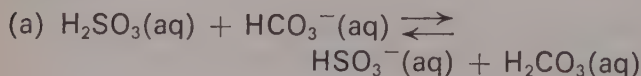
The reaction favors products, but very little, since the K 's are nearly the same.

Problem 22

Write the equations for the reactions between each of the following acid-base pairs. For each reaction, predict whether reactants or products are favored.



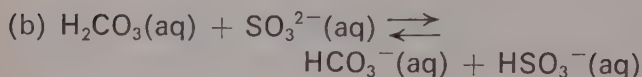
Answer



$$K_A(\text{H}_2\text{SO}_3) = 1.7 \times 10^{-2}$$

$$K_A(\text{H}_2\text{CO}_3) = 4.4 \times 10^{-7}$$

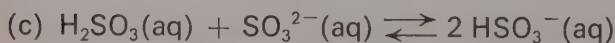
Products favored.



$$K_A(\text{H}_2\text{CO}_3) = 4.4 \times 10^{-7}$$

$$K_A(\text{HSO}_3^-) = 6.2 \times 10^{-8}$$

Products favored, but very little.



$$K_A(\text{H}_2\text{SO}_3) = 1.7 \times 10^{-2}$$

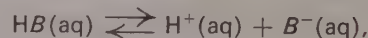
$$K_A(\text{HSO}_3^-) = 6.2 \times 10^{-8}$$

Products favored.

Problem 23

A 0.25 M solution of benzoic acid (symbolize it HB) is found to have $[\text{H}^+] = 4 \times 10^{-3} M$.

Assuming the simple reaction



calculate K_A for benzoic acid.

Answer

Since the only source of $\text{H}^+(\text{aq})$ gives an equal amount of $\text{B}^-(\text{aq})$, we can write $[\text{H}^+] = [\text{B}^-]$. Furthermore, the amount of $\text{H}^+(\text{aq})$ formed is negligible compared to 0.25 M . Hence

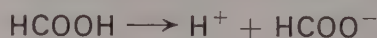
$$K_A = \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]} = \frac{[\text{H}^+]^2}{[\text{HB}]} = \frac{(4 \times 10^{-3})^2}{(0.25)} \\ = \frac{16 \times 10^{-6}}{0.25} = 6.4 \times 10^{-5}$$

Problem 24

If 23 grams of formic acid, HCOOH , are dissolved in 10.0 liters of water at 20°C , the $[\text{H}^+]$ is found to be $3.0 \times 10^{-3} M$. Calculate K_A .

Answer

If the concentrations are known, we can determine K_A in the following manner:



$$K_A = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

We know that $[\text{H}^+] = 3.0 \times 10^{-3} M$.

We also know that $[\text{HCOO}^-] = [\text{H}^+]$.

We can find $[\text{HCOOH}]$ as follows:

$$\frac{23 \text{ g}}{10 \text{ liter}} \times \frac{1 \text{ mole}}{46 \text{ g}} = (0.50) \left(\frac{\text{mole}}{10 \text{ liter}} \right) = 0.050 \frac{\text{mole}}{\text{liter}}$$

Since $[\text{H}^+] = 3.0 \times 10^{-3}$, and since all this came from HCOOH , the $[\text{HCOOH}]$ must change from 0.050 to $(0.050 - 0.0030) = 0.047 M$. Then

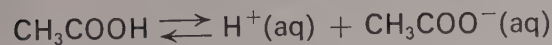
$$K_A = \frac{(3.0 \times 10^{-3})^2}{4.7 \times 10^{-2}} = 1.9 \times 10^{-4}$$

Problem 25

A chemist dissolved 30 grams of CH_3COOH in enough water to make one liter of solution. What is the concentration of this acetic acid solution? What is the concentration of $\text{H}^+(\text{aq})$? Assume a negligible change in $[\text{CH}_3\text{COOH}]$ because of dissociation of $\text{H}^+(\text{aq})$.

Answer

$$\frac{30 \text{ g}}{\text{liter}} \times \frac{1 \text{ mole}}{60 \text{ g}} = 0.5 \frac{\text{mole}}{\text{liter}} \text{ or } 0.5 M$$



$$K_A = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

Let $y = [\text{H}^+]$. Then,

$$[\text{H}^+] = [\text{CH}_3\text{COO}^-] = y$$

$$[\text{CH}_3\text{COOH}] = 0.5 - y$$

Since we may ignore y , we may write

$$\frac{y^2}{0.5} = 1.8 \times 10^{-5}$$

$$y = \sqrt{9 \times 10^{-6}} = 3 \times 10^{-3} M = [\text{H}^+]$$

Problem 26

- (a) Nitric acid is a very strong acid. What is $[\text{H}^+]$ in a $0.050 M \text{HNO}_3$ solution?
- (b) Hydrogen peroxide, H_2O_2 , is a very weak acid. What is $[\text{H}_2\text{O}_2]$ in $0.050 M \text{H}_2\text{O}_2$ solution?

Answer

- (a) Since HNO_3 is a very strong acid, products are much favored, and practically all of the acid is in the form of ions, $\text{H}^+(\text{aq})$ and $\text{NO}_3^-(\text{aq})$. Therefore $[\text{H}^+] = 0.050 M$.
- (b) Since H_2O_2 is a very weak acid, reactants are much favored, and practically all of the acid is in the form of undissociated acid, $\text{H}_2\text{O}_2(\text{aq})$. Therefore $[\text{H}_2\text{O}_2] = 0.050 M$.

Problem 27

A water solution that contains $0.10 M \text{HF}$ is 8% dissociated. What is the value of its K_A ?

Answer: 6.9×10^{-4} .

Answer

	$\text{HF}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{F}^-(\text{aq})$			
Initial conc.	0.10	0	0	<i>M</i>
Equil. conc.	0.092	0.008	0.008	<i>M</i>

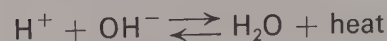
$$K_A = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{(0.008)^2}{(0.092)} = \frac{64 \times 10^{-6}}{9.2 \times 10^{-2}} = 6.9 \times 10^{-4}$$

Problem 28

Is the reaction $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{H}_2\text{O}$ exothermic or endothermic? Use your answer and Le Chatelier's Principle to decide whether K_w increases or decreases with increasing temperature.

Answer

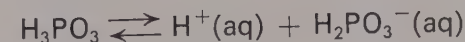
Exothermic. Experiment 31 showed this. The full equation is



Thus, an increase in temperature will yield more ions and a larger K_w .

Problem 29

A solution containing $0.20 M \text{H}_3\text{PO}_3$, phosphorous acid, is tested with indicators and the $\text{H}^+(\text{aq})$ concentration is found to be $5.0 \times 10^{-2} M$. Calculate the K_A of H_3PO_3 , assuming that a second proton cannot be removed.

Answer

$$K_A = \frac{[\text{H}^+][\text{H}_2\text{PO}_3^-]}{[\text{H}_3\text{PO}_3]}$$

$$[\text{H}^+] = [\text{H}_2\text{PO}_3^-] = 5.0 \times 10^{-2} M$$

$$[\text{H}_3\text{PO}_3] = 0.20 - 0.050 = 0.15 M$$

$$K_A = \frac{(5.0 \times 10^{-2})(5.0 \times 10^{-2})}{(0.15)} = 1.7 \times 10^{-2}$$

Note: The second dissociation constant is 7×10^{-7} , hence this reaction forms only a negligible amount of H^+ and HPO_3^{2-} . Note also that the dissociation of H_3PO_3 cannot be neglected in estimating its concentration.

Suggested Quiz Problems

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

1. Which one of the following properties would a solution have if it is an acid?

- (1) Solution turns litmus blue.
- (2) Solution tastes bitter.
- (3) Solution has a hydrogen ion concentration of $10^{-13} M$.
- (4) Solution is a very good conductor of electricity.
- (5) Solution feels slippery.

Answer: (4).

2. Which one of the following would be possible for both strongly acidic and strongly basic solutions?

- (1) Solution has a hydrogen ion concentration of $10^{-7} M$.
- (2) Solution turns litmus red.
- (3) Solution tastes sour.
- (4) Solution is a very good conductor of electricity.
- (5) Solution reacts with Mg to liberate hydrogen.

Answer: (4).

3. If an unknown solution is known to be either dilute nitric, hydrochloric, or sulfuric acid, it can be positively identified as sulfuric acid by adding which of the following?

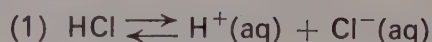
- (1) $NH_3(aq)$ to obtain $NH_4^+(aq)$.
- (2) An indicator to determine the $[H^+]$.
- (3) A drop of $AgNO_3$ solution to see if a precipitate forms.
- (4) CH_3COONa solution to form $CH_3COOH(aq)$.
- (5) $Ba(NO_3)_2$ solution to see if a precipitate forms.

Answer: (5).

4. Given a $0.1 M$ HCl solution,

- (1) What is the $[H^+]$?
- (2) What is the $[OH^-]$?

Answer



If we assume HCl to be 100% dissociated, then

$$[H^+] = 0.1 \text{ mole/liter}$$

$$(2) K_w = [H^+][OH^-] = 10^{-14}$$

Thus

$$[OH^-] = \frac{10^{-14}}{10^{-1}} = 10^{-13} \text{ mole/liter}$$

5. Given a $0.01 M$ $NaOH$ solution,

- (1) What is the $[OH^-]$?
- (2) Calculate the $[H^+]$.

Answer

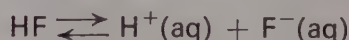
- (1) If we assume the $NaOH$ to be 100% dissociated, then

$$[OH^-] = 10^{-2} \text{ mole/liter}$$

$$(2) [H^+][OH^-] = 10^{-14}$$

$$[H^+] = 10^{-12} \text{ mole/liter}$$

6. The $[H^+]$ of a $0.1 M$ solution of a weak acid, HF , is found to be $8.2 \times 10^{-3} M$. Let the following equation represent the reaction between the weak acid and water.



- (1) What is the concentration of the fluoride ion, $F^-(aq)$?
- (2) Write the expression for the equilibrium constant, K_A , and find its numerical value.

Answer

$$(1) [H^+] = [F^-] = 8.2 \times 10^{-3} \text{ mole/liter}$$

$$\begin{aligned} (2) K_A &= \frac{[H^+][F^-]}{[HF]} \\ &= \frac{(8.2 \times 10^{-3})(8.2 \times 10^{-3})}{10^{-1}} \\ &= 6.7 \times 10^{-5} \end{aligned}$$

7. Four grams of $NaOH(s)$ are dissolved in just enough water to make 1 liter of solution.

- (1) What is the molar concentration of the solution?

SUGGESTED QUIZ QUESTIONS

- (2) What is the $[\text{OH}^-]$?
 (3) What is the $[\text{H}^+]$?

Answer

$$(1) \frac{4 \text{ g/liter}}{40 \text{ g/mole}} = 0.1 \text{ } M$$

$$(2) [\text{OH}^-] = 0.1 \text{ mole/liter} = 0.1 \text{ } M$$

$$(3) [\text{H}^+] = \frac{10^{-14}}{10^{-1}} = 10^{-13} \text{ } M$$

8. Calculate $[\text{H}^+]$ in solutions made by mixing 100 ml 1.00 M HNO_3 with

- (1) 100 ml 0.100 M KOH ,
 (2) 100 ml 0.990 M KOH ,
 (3) 100 ml 1.010 M KOH .

Answer

- (1) In each solution the molarity will be halved.

$$\text{Initial } [\text{H}^+] = 0.500$$

$$\text{Initial } [\text{OH}^-] = 0.050$$

$$\text{Final } [\text{H}^+] = 0.500 - 0.050 = 0.450$$

- (2) Again the molarities will be halved

$$\text{Initial } [\text{H}^+] = 0.500$$

$$\text{Initial } [\text{OH}^-] = 0.495$$

$$\text{Final } [\text{H}^+] = 0.500 - 0.495 \\ = 0.005 = 5 \times 10^{-3}$$

- (3) Again the molarities will be halved.

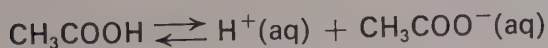
$$\text{Initial } [\text{H}^+] = 0.500$$

$$\text{Initial } [\text{OH}^-] = 0.505$$

$$\text{Final } [\text{OH}^-] = 0.505 - 0.500 = 0.005$$

$$[\text{H}^+] = \frac{10^{-14}}{5 \times 10^{-3}} = 2 \times 10^{-12} \text{ } M$$

9. Consider the reaction



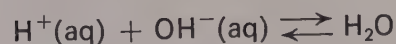
Using Le Chatelier's Principle decide whether $[\text{H}^+]$ will be larger or smaller if sodium acetate, NaCH_3COO , is dissolved in the reaction mixture. Justify your answer.

Answer

The $[\text{H}^+]$ will be smaller. When NaCH_3COO dissolves, it will increase $[\text{CH}_3\text{COO}^-]$. This will disturb the equilibrium condition, and a partially nullifying action will take place to reduce $\text{CH}_3\text{COO}^-(\text{aq})$. Such action will use up $\text{H}^+(\text{aq})$.

10. How many milliliters of 0.02 M HCl are needed to react completely with 100 ml of 0.01 M NaOH ?

Answer



One mole of HCl reacts with one mole of NaOH .

$$\frac{100 \text{ ml}}{1000 \text{ ml/liter}} \times \frac{0.01 \text{ mole}}{\text{liter}} \\ = 0.001 \text{ mole NaOH}$$

The 0.001 mole of NaOH will require 0.001 mole of HCl . The required amount of HCl to contain 0.001 mole is

$$\frac{0.001 \text{ mole}}{0.02 \text{ mole/liter}} \times \frac{1000 \text{ ml}}{\text{liter}} = 50 \text{ ml HCl}$$

11. If 100 ml of 0.020 M HNO_3 are added to 100 ml of 0.110 M $\text{Ba}(\text{OH})_2$, what is $[\text{H}^+(\text{aq})]$ at equilibrium in the resulting solution?

Answer

The molarity of both solutions will be halved.

$$\text{Initial } [\text{H}^+] = 0.010$$

$$\text{Initial } [\text{OH}^-] = 0.110$$

$$\text{Final } [\text{OH}^-] = 0.110 - 0.010 = 0.100 \text{ } M$$

$$\text{Since } [\text{H}^+][\text{OH}^-] = 10^{-14},$$

$$[\text{H}^+] = \frac{10^{-14}}{10^{-1}} = 10^{-13}$$

Oxidation and Reduction



Intent and Approach

Chapter 15 bears a rather strong resemblance to Chapter 14 in general form. We again start from a group of relatively simple observations involving easily measured phenomena (i.e., cell potentials); we look for a means of systematizing the observations; we adopt rather arbitrary definitions such as those for oxidizing agent, acid, oxidation number, etc.; then we systematize the values (table of E° values) and use the concepts we have defined to make predictions which can be tested by experiment. As mentioned in the background section, sometimes our predictions are valid (for example, in the reaction of HI and Zn), and sometimes they are wrong, as in the reaction between HI and Ag. If our predictions are wrong, we have extended our model beyond its limit of applicability, and we must look for the new variable which has become important but which was neglected in our original treatment.

In general, the definitions of oxidation, reduction, anion, cation, anode, and cathode are much more standardized than are the definitions of acid and base. We still find, however, that this chapter abounds in arbitrary conventions such as the sign of E° for a process, the rules for calculating oxidation number, etc. Fortunately the rules are quite generally accepted, but this does not render them less arbitrary. Above all, they are *very useful*.

Try to point out to the student the difference

between convention, model, and experimental fact. Electric current flows from one electrode to another; this is a fact. We picture the process that generates the current in terms of half-cell reactions at each electrode; this is our model. We call the electrode at which a loss of electrons is assumed to occur the anode; this is a convention. The first point is not subject to debate or compromise; it comes from observations. The second point, involving the model, is consistent with the facts but is not unique. We can assume other models that will explain the observations. For example, charge distribution in chemical species may not be the same as that indicated in our half-cell reactions at all. The processes of electron transfer could conceivably be quite different from those that we are writing. In the reduction of permanganate ion we say the oxidation number of Mn is +7, yet no one believes that manganese actually carries this charge. A convention, such as our definition of an anode, is the most arbitrary of all and is usually closely related to the model we have chosen.

In this chapter we balance oxidation-reduction reactions by using inspection or half-cell reactions. Oxidation number is presented but not used in the Textbook as a balancing method. A good start is made if you wish to use this technique.

Outline

The process occurring in an electrochemical cell is analyzed in terms of two half-cell reactions. Loss and gain of electrons in half-reactions (15-1) is presented as one kind of oxidation and reduction.

Concepts developed for half-cells are applicable to electrochemical processes occurring in a single solution (15-2) and are illustrated by examples.

Many oxidation-reduction processes are conveniently considered in terms of competition for electrons (15-3). A more detailed analysis of the electrochemical cell permits us to evaluate electron competition in terms of cell voltage.

Section 15-4 develops the water analogy for electrical units. It serves as introduction for subsequent sections.

In Section 15-5 we learn that *the voltage of a cell* indicates whether reactants or products will be favored at equilibrium. The voltage is dependent upon concentration. Voltages for different cells are additive. This observation

leads to the recognition of *half-cell potentials* which can be added to give cell potentials.

Half-cell potentials may be conveniently measured and tabulated if certain arbitrary experimental conventions are accepted [the H_2 half-cell is 0.00 volt, and values are reported for unit concentration (or activity)] (15-5).

The table of half-cell potentials permits us to predict equilibrium conditions and cell voltages (15-6).

Storage batteries, electrochemical cells, and corrosion provide some practical examples of electrochemistry (Sections 15-7 and 15-8).

Electrolysis is discussed briefly (15-9) and made quantitative by means of the Faraday (15-10).

The balancing of oxidation-reduction reactions is discussed using the half-cell and inspection methods (15-11).

Section 15-12 introduces oxidation numbers and stresses their arbitrary nature.

Section 15-13 is a review.

New Concepts

1. The half-cell reaction, as it is applied in a description of an electrochemical cell.
2. Electron transfer, as one way to express oxidation and reduction.
3. Cell potentials and competition for electrons.
4. Tables of oxidation potentials and their use in predicting reactions.
5. Balancing oxidation-reduction equations.
6. The meaning of oxidation number.

SCHEDULE AND RELATED MATERIAL

Suggested Time : 13 days

Text Section	Topic and Other Work	Exercises	Problems		
			Easy	Medium	Hard
	Expt. 34. Introduction to Oxidation-Reduction				
15-1	Electrochemical Cells		1	2-4	5
15-2	Oxidation-Reduction in a Beaker		6	7, 8	
15-3	Competition for Electrons <i>Film:</i> Electrochemical Cells	1			9
15-4	Volts, Amperes, and Coulombs		10	11-13	
15-5	Voltage of a Cell and Tendency to Release Electrons			25	17
15-6	Predicting Redox Reactions <i>Film:</i> Nitric Acid	2-5	21-24	14, 15, 18	16, 19, 20
15-7	Storage Batteries and Electrochemical Cells		33		
	Expt. 35. Corrosion of Iron				
15-8	Corrosion of Iron				
15-9	The Electrolytic Process	6			
	Expt. 36. Electroplating Copper and Silver				
15-10	Quantitative Relations in Electrolysis		32	31	26, 34-36
15-11	Balancing Oxidation-Reduction Equations	7-9		28-30	
15-12	Oxidation Numbers	10, 11		27	
15-13	Review				

Development

Expt. 34, INTRODUCTION TO OXIDATION-REDUCTION,

fits here. See p. 194 in the Laboratory Guide.

15-1 The Chemistry of Electrochemical Cells

The central theme of the entire chapter is systematization of experimental observations through

construction of a useful but somewhat arbitrary formalism. In this section we are concerned with the development of the experiments which form the background for the entire chapter. You can help by demonstrating the Cu-Ag cell described on pages 278-280. Tie the actual equipment to Figures 15-1 and 15-2. Then, later, make sure the student sees that the schematic version in Figure 15-3 is the same as the apparatus. The simplified drawings will be used throughout.

Another object of the demonstration is to show one definition of oxidation in terms of electron loss. You may find it helpful to point out that the word oxidation arises from processes involving combination with oxygen. The burning of Mg in O_2 is easily identified as oxidation. The elements Mg and O_2 combine to give Mg^{2+} and O^{2-} in an NaCl-type lattice. When Mg is oxidized, Mg^{2+} is formed from Mg by *loss* of electrons. We can now generalize in a rather formal sense.

This section is also important for establishing some terms.

For example, by carefully avoiding the convention of assigning a sign to either electrode we can sidestep a problem which frequently bothers students—namely, the positive ions move toward the “positive” electrode, and the negative ions move toward the “negative” electrode. This problem can be troublesome and yields little; avoid placing it before the student if possible.

The nomenclature used in oxidation-reduction reactions can be confusing. Here are two mnemonic devices that may help.

- (1) Anions are negative ions.

A N I O N S
r e o
e g n
a s
t
i
v
e

- (2) Oxidation occurs at the
Anode
(vowels together)

Reduction occurs at the
Cathode
(consonants together)

Emphasize that *the voltage of a cell* indicates the conditions that prevail at equilibrium. We need this concept in the following sections.

15-2 Oxidation-Reduction Reactions in a Beaker

Point out that the reaction between copper and silver nitrate was carried out under rather specialized conditions in 15-1 but that the reaction will go equally well in an ordinary beaker. We still find it *convenient* to use the ideas about half-cell reactions which we developed in 15-1. The names and ideas are still applicable. Our observations and formalism are thus extended somewhat beyond the original experiments.

The reaction of Zn and H^+ , used to characterize an acid experimentally, is easily interpreted in terms of oxidation and reduction. Our formal schemes meet on a common experimental ground. Stress the experimental aspects of this whole section; remember that we do experiments to get the facts which we will later arrange in a systematic fashion. The experiments are easy to do and to interpret. That is, it is not hard to find out which reactants will give which products under a given set of conditions.

15-3 Competition for Electrons

We picture two metals competing for *electrons*, and we list the metals in order of their ability to *release* electrons. Again note that in doing this we are systematically arranging *observed* facts. Gradually a table of such relations is built up. It expresses a regularity. From the table, we can make useful predictions, just as we did for acids. The list developed in this section is qualitative; our quantitative list comes later.

Film, ELECTROCHEMICAL CELLS,

fits here. See p. 301 for summary.

15-4 Volts, Amperes, and Coulombs

This section is to give some meaning to the three terms used for measuring electricity. The students probably know the first word, volts, but may be hazy on its meaning. The familiar water pressure-water flow analogy is used. It may be interesting that the electrical terms are

all named in honor of scientists who studied electricity.

15-5 The Voltage of an Electrochemical Cell and the Tendency to Release Electrons

This section begins with separate comparisons of two half-cells with the hydrogen reference half-cell. The question of partitioning a measured physical quantity such as a cell voltage between two components to get values for two imagined parts (half-cells in this instance) is a common and difficult one in chemistry. We face the same type of problem in measuring ionic radii, ionic heats of solution, and a number of other quantities. Various means are used to solve the problem; in this particular situation, we *arbitrarily* decide to set the value of the half-cell $\text{H}_2 \rightleftharpoons 2 \text{H}^+ + 2 e^-$ at 0.00 volt and compare all other values to it. This is a *convenient* and *arbitrary* convention. It has no absolute significance.

Some precautions are needed in adding half-cell values in special situations. Specifically, the number of electrons involved in each reaction being added must be the same. For example, see the background section, page 304, for the way to obtain the value for $\text{Cr} \longrightarrow \text{Cr}^{3+} + 3 e^-$ from values for $\text{Cr} \longrightarrow \text{Cr}^{2+} + 2 e^-$ and $\text{Cr}^{2+} \longrightarrow \text{Cr}^{3+} + e^-$.

Stress the utility of Le Chatelier's Principle in considering the effects of concentration on cell voltage. Since the voltage indicates equilibrium conditions and since concentration changes alter equilibrium conditions, concentration changes should have a *predictable* effect upon voltage. The illustration of a flashlight dry cell might be useful. The voltage is high when concentrations are far from the run-down, or *equilibrium*, condition of the cell, but *the voltage gradually drops until it is zero when the equilibrium concentrations have been reached*. Since concentration is an important variable in determining voltage, we must arbitrarily fix the concentration values for all cell components if a realistic comparison of E° values for different reactions is to be made. For this reason, E° values listed later in tables are based on a cell in which the *effective concentration* of

each ion at the solid electrode surface is one mole/liter. Using this convention we can compare different chemical processes under conditions arranged such that concentration is not a variable. The details of measurement come later.

Don't become confused with signs. It is generally agreed that a positive value of E° indicates that for the equation as written (e.g., $\text{Zn} \rightleftharpoons \text{Zn}^{2+} + 2 e^-$; $E^\circ = +0.76$ volt) products will be more abundant at equilibrium than reactants. If the equation is turned around and written $\text{Zn}^{2+} + 2 e^- \rightleftharpoons \text{Zn}$, then E° for the process as now written is *negative*. This means the reactants will predominate at equilibrium. Make it well known that Textbook Table 15-2 applies only to solutions in which the ionic species are 1 *M*. This convention is followed almost universally.

Use several practice questions to make sure the students can correctly calculate the net E° value for a given equation. This skill is needed throughout the remainder of this chapter and is used frequently in later, descriptive chapters.

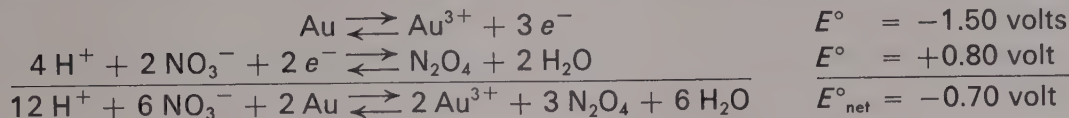
Problem 17, or one like it, is useful to stress that the choice of zero voltage for the hydrogen half-reaction does not affect the net cell potential values.

15-6 Predicting Redox Reactions

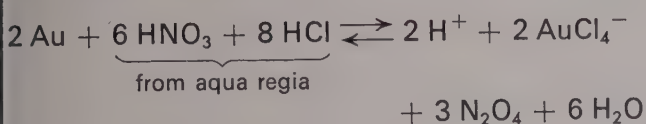
Considerable drill will also be helpful in fixing the main point of this section. If E° for the overall process is positive, products predominate at equilibrium when concentrations are reasonably close to those used in establishing the table. If E° is negative, reactants predominate at equilibrium. If E° is zero, the process is at equilibrium when concentrations are those used in the table. The student should be able to use Table 15-2 with facility.

All is not gold that glitters! Sometimes, variables such as concentration may differ significantly from those used in establishing the table. Predictions made from the table without considering other factors may therefore be wrong. The reaction of Ag and H^+ given in this section is such an example; another is the action of HBr on copper, $2 \text{HBr} + \text{Cu} \rightleftharpoons \frac{1}{2} \text{H}_2 + \text{H}^+ + \text{CuBr}_2^-$.

Another is the dissolution of gold by aqua regia. The E°_{net} value for the action of HNO_3 on gold



However the concentration of Au^{3+} is reduced by the formation of the complex ion AuCl_4^- . The reaction does occur.



The E° value which must be considered is that for actual processes which take place. These may differ from the obvious entries in the table. Other more complex examples appear in the background section. Systems of correlation don't replace the need for thought and experimentation.

Since we have hinted that E° is related to the equilibrium state and that K measures the same thing, some student may expect a relation between E° and K . The background gives it without the thermodynamic derivation, which is too advanced for usefulness at this time.

Film, NITRIC ACID,

fits here. See p. 301 for summary.

SPONTANEOUS REDOX REACTIONS

15-7 Storage Batteries and Electrochemical Cells

This section gives some applications of the reactions studied earlier. Indicate how economic and practical factors apply. Thus, any pair of half-reactions from Table 15-2 could be made into a battery. But some are better or cheaper than others. A good battery should be cheap, long-lasting, easy to regenerate, produce much energy per kilogram of mass, maintain a steady voltage, produce no noxious substances, and operate over a wide range of temperature and

is negative. The process does not tend to proceed as written (for the standard concentrations).

pressure conditions. Some of the current surge of interest in new batteries is aimed at improving the power/mass ratio of the lead-lead oxide cell. It is too heavy for space vehicles or electric powered cars. See *Supplementary Materials*.

Fuel cells represent a further attempt to increase the efficiency of fuel use. These devices have achieved some success in laboratory models. So far large scale uses have not been worked out.

Expt. 35, CORROSION OF IRON,

fits here. See p. 198 in the Laboratory Guide.

15-8 Corrosion of Iron, an Undesirable Redox Reaction

This section shows how electrochemical action can destroy a metal (corrosion) or protect it by interposing another source of electrons (cathodic protection).

Rusting of iron is not a simple reaction of iron plus oxygen to give iron oxide. It is best to follow the Textbook's lead and avoid writing an equation. Just describe what happens and how these observations can be explained. In case you do write an equation, make sure you explain that it does not show mechanism.

NONSPONTANEOUS REDOX REACTIONS

15-9 The Electrolytic Process

Here, another practical use of the information in Table 15-2 is given. Material in this section can be related conveniently to the material about cells (Section 15-5). Refer back to that discussion before you consider Section 15-9.

Electrolysis is used in a number of ways. Purification of metals is described. The next

section tells of the production of sodium, chlorine, magnesium, and aluminum. Some other chemicals made electrochemically are KMnO_4 , paint pigments such as white lead (basic lead carbonate) and chrome yellow (lead chromate), H_2O_2 , F_2 , NaOH , and H_2 . A few organic substances are also oxidized or reduced electrically. Some of the products are sorbitol (from glucose), hydrocarbons (from ketones), and alcohols (from aldehydes and ketones). One advantage of the electrolytic method is its selectivity. By careful control of voltage, unwanted reactions can be suppressed.

Electroplating is a second major use of electrolysis. This is just the same as the copper purification example except the metal is plated on an object made of a different metal. Electroplating is done for beauty or for protection against corrosion. The two examples the student knows best are chromium-plated trim on automobiles and tin-plated steel for "tin cans." Jewelry and eating utensils are often silver-plated and many nonrusting nuts and bolts are cadmium-plated.

Electromachining or electroforming is, in a sense, the reverse of electroplating. Electromachining uses the dissolving action at the anode instead of the plating action of the cathode. By chemical action metals or alloys that are difficult to machine can be shaped to close tolerances. Very thin pieces can be made without stress in them, often with a finely polished surface, in a single operation. Some substances shaped this way are beryllium, tungsten, and molybdenum parts for jet engines.

**Expt. 36, MOLES OF COPPER,
MOLES OF SILVER, AND
MOLES OF ELECTRONS INVOLVED
DURING ELECTROLYSIS,**

fits here. See p. 202 in the Laboratory Guide.

15-10 Quantitative Relations in Electrolysis

The full significance of Faraday's Laws emerges when they are interpreted in terms of the atomic

theory. If electric charge can "count" atoms (as Faraday's Laws imply), then electric charge must come in "packages." From this notion it is only a step to that of associating the unit charge with a fundamental particle.

Experiment 36 gives the student the opportunity to verify a Faraday Law. These relations of Faraday provide a way to connect quantity of electricity to mass. Along with this they illustrate again the change of energy from one form (electrical) to another (chemical).

15-11 Balancing Oxidation-Reduction Equations

There is no single correct method for balancing redox equations. Three methods are outlined here. The procedures in each need no amplification; they are founded on the conservation of charge and mass in a real process. If the example is simple enough, inspection suffices. Otherwise, combining equations for half-reactions leads to a balanced overall equation.

Throughout this section, remind the student that balancing the equation is not an end in itself. It is done to express correctly the experimental facts: mass is conserved, charge is conserved, and certain reactants give certain products. Other schemes for determining the numbers needed to conserve mass and charge are available. See the *Background Discussion*.

15-12 Oxidation Numbers

Oxidation numbers provide a convenient way to refer to the chemical state of elements. It becomes particularly useful for transition elements which have several common states. The Stock system of naming depends on using oxidation numbers. A beginning student can also use these numbers to decide whether oxidation or reduction has taken place in a reaction. When the oxidation number becomes more positive that atom has been oxidized. Finally oxidation numbers are often used in balancing redox equations. The *Background Discussion* contains an example.

The arbitrary nature of oxidation numbers

deserves some comment. Especially numbers for elements in oxygenated or complex ions. A Na^+ ion in molten NaCl very likely has lost an electron. It is unlikely that a Mn atom in MnO_4^- has lost 7; although the oxidation number

is +7. Note we have placed the plus (or minus) sign before the numeral in oxidation numbers. It is after the numeral in ionic charge symbols.

15-13 Review

Supplementary Material

Films

For ordering information see the *List of Film Sources* at the back of the Teacher's Guide.

NITRIC ACID

A CHEM Study film

Running Time: 18 minutes

This film, made in collaboration with Dr. H. H. Sisler, uses the chemistry of nitric acid to review concepts of Chapters 12–15. The film shows the manufacture and use of HNO_3 , but also illustrates the value of Le Chatelier's Principle, reaction rate considerations, and K and E° .

ELECTROCHEMICAL CELLS

A CHEM Study film

Running Time: 22 minutes

Equilibrium in an electrochemical cell is the central idea of this film. Experiments and animation illustrate the migration of ions and the electron flow in a silver–copper cell. The effect of changing concentrations of the reacting species is demonstrated in a silver–hydrogen cell and explained with animation. Prof. J. A. Campbell, of Harvey Mudd College, and June S. Ewing, CHEM Study Staff, collaborated on this film.

Articles

"The Electric Automobile," *Scientific American*, Oct. 1966, pp. 34–40. This article shows one of the newer batteries and gives some arguments for electric cars.

Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Ed., John Wiley, N. Y., 1963–6, Vol. 3, pp. 98–270. Great detail on batteries. Fuel cells are treated on pp. 139–159.

Background Discussion

OXIDATION-REDUCTION REACTIONS

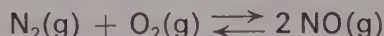
The burning of Mg in O_2 (traditional oxidation) to give Mg^{2+} and O^{2-} in a lattice of the sodium chloride type (Mg^{2+} ions replace Na^+ , and O^{2-} replace Cl^-) might be cited to establish a rationale for one definition of this chapter. If electrons are lost in a reaction, oxidation is said to have occurred; if electrons are gained in a reaction, reduction is said to have occurred. If our use of electrochemical cells to introduce oxidation-reduction seems strange in view of your past experience, you might consider any alternative procedures by which one could accumulate *quantitative* experimental information

on this topic so easily. Remember that an electrochemical cell is simply an oxidation-reduction process carried out under special conditions. The systematization of the data so obtained is our basic objective.

THE DEFINITIONS OF OXIDATION-REDUCTION

You will notice the Textbook and Guide have been careful *not* to say flatly that "oxidation is the loss of electrons" or, more generally, that oxidation-reduction is the transfer of electrons. In addition, there is the implication, "oxidation-reduction is a change in oxidation number." We

treat these concepts cautiously because reactions exist that everyone will agree are examples of oxidation, but in which there is a real question whether any electrons were transferred. Examine the reaction



You cannot argue that nitrogen gave any electrons to oxygen, because the dipole moment of NO is so low (0.15D). To allow for this type of reaction, use both concepts discussed, and indicate that *each* is just one kind of description of oxidation-reduction.

THE THERMOCHEMICAL ASPECTS OF CELL OPERATION

In our earlier discussions (pp. 252 and 253), we noted that the balance between stability and randomness determines whether a reaction occurs spontaneously. We represented the balance by the equation

$$\log K = \frac{2 \times 0.03}{0.0591} = \frac{2 \times 0.03}{0.06} = 1$$

$$K = 10^1 = 10$$

This value of K is commensurate with the observation that there is not a tremendous excess

Substitution in the equation for K gives

$$\log K = \frac{2 \times 1.10}{0.0591} = 35.5$$

$$K = 10^{35.5}$$

$$\Delta G = \Delta H - T\Delta S$$

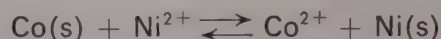
and called ΔG the free energy. A spontaneous process at constant pressure and temperature has a negative value of ΔG .

We can use the relation between E° and K to show some quantitative calculations. Use the equation

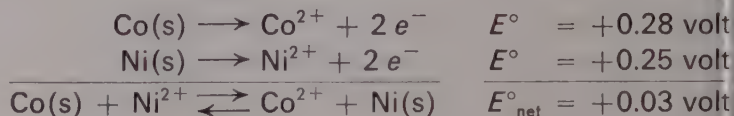
$$\log K = \frac{nE^\circ}{0.0591}$$

which is valid at 25°C, the temperature for which we gave our E° data. In this equation, n equals the number of electrons involved in each half-cell reaction when they are ready to sum for the net cell equation.

We will now apply this equation to the reaction presented in Section 15-3. This reaction reaches a state of equilibrium when rather large amounts of both reactants and products are present.

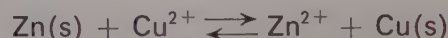


From Table 15-2 we find

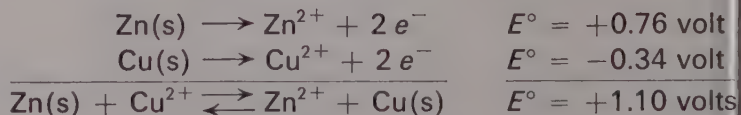


of products or of reactants at equilibrium.

By way of contrast, let us calculate K for this reaction,



for which we found experimentally that the state of equilibrium greatly favored the products. From Textbook Table 15-2 we get

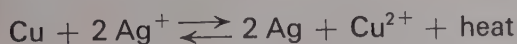


or approximately 3×10^{35} . This very large value of K agrees with our experimental observations.

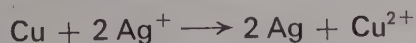
Since values of E° (Chapter 15) as well as values of K (Chapter 13) indicate the conditions at equilibrium, it seems logical that they should

be related to the value of ΔG . This expectation is realized if we consider a process under rather specific conditions.

Simple inspection of the equation



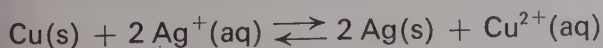
and an application of Le Chatelier's Principle indicate that a large concentration of Ag^+ and a small concentration of Cu^{2+} should increase the tendency for the process



to occur. It would seem obvious, then, that ΔG could be used to compare the equilibrium states for a series of chemical processes *only* if we reached some agreement relative to concentration in each process. Since E° was defined in terms of unit concentrations of ions, it seems logical to compare ΔG values when all effective concentration terms are also set equal to unity (1 mole/liter) and all effective gas pressures are set at one atmosphere. The value of ΔG measured under these conditions is designated ΔG° , which is related to the equilibrium constant for the system by the equation

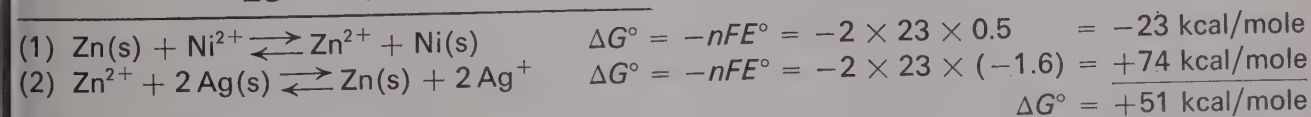
$$\Delta G^\circ = -RT \ln K = -(RT)(2.303 \log K)$$

where K is the value of the equilibrium constant, R is the gas constant ($2 \text{ cal mole}^{-1} \text{ deg}^{-1}$), and T is the absolute temperature. For the process

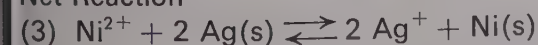


we can write $\Delta G^\circ = -2.303 RT \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$. Free energy change, ΔG° , is related to the E° value for the above process by the expression

$$\Delta G^\circ = -nFE^\circ$$



Net Reaction



$$-E^\circ = \frac{+51}{2 \times 23}$$

$$E^\circ = -1.1 \text{ volts}$$

where n = the number of moles of electrons transferred in the reaction as written and F = the value of the Faraday (96,500 coulombs, or 23,000 cal/volt $\times$ moles of electrons).

Since the expressions for both K and E° are equated to ΔG° , we can write

$$2.303 RT \log K = nFE^\circ$$

$$\begin{aligned} \log K &= nE^\circ \times \frac{F}{2.303 \times RT} \\ &= nE^\circ \times \frac{23,000}{2.303 \times 2 \times 298} \\ \log K &= \frac{nE^\circ}{0.0591} \end{aligned}$$

The above relationship is interesting and provides a direct connection between K and E° , but it is not of as much importance for the subject matter of this chapter as is the basic relationship between ΔG° and E° :

$$\Delta G^\circ = -nFE^\circ$$

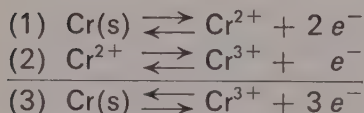
Let us explore the nature of ΔG° by reviewing information we have about ΔH . The value of ΔH depends upon the quantity of materials taken. It depends only upon the initial and final states of the system; it varies with temperature; and it can be added when we add the equations for the processes (see p. 200). As might have been guessed from the similarity between ΔG and ΔH in the equation for ΔG , it is clear that ΔG also has all the characteristics shown by ΔH .

The property of additivity is especially important. By way of illustration, let us calculate the E° value of a reaction from two others.

Note two things about these equations. First, because the value for ΔG° of the net reaction is positive and the value for E° is negative, we know that the process is not spontaneous. The conclusion checks with all of our experience. Second, we have multiplied the E_1° and E_2° values by nF , added these ΔG° values, and then divided the sum again by nF to get E_3° of the overall process

$$\begin{aligned}\Delta G_3^\circ &= \Delta G_1^\circ + \Delta G_2^\circ \\ -nFE_3^\circ &= -nFE_1^\circ - nFE_2^\circ\end{aligned}$$

As the above relation shows, we could have canceled the nF factor and simply added E_1° and E_2° values to get E_3° . *The addition of E° values is legitimate whenever the values of nF will cancel out.* This is true either in adding half-cell potentials to get overall cell potentials or in adding two overall cell potentials. *There are several circumstances, however, in which nF values don't cancel out and in which we must add ΔG values, not E° values.* Consider the following example. We have E° values for the two half-reactions, labeled 1 and 2 below, and we want the E° value for the reaction labeled 3.



The observed potentials are 0.91, 0.41, 0.74 volt reading down. Note that $E_1 + E_2$ does not equal E_3 . However,

$$\Delta G_1^\circ + \Delta G_2^\circ = \Delta G_3^\circ$$

$$\begin{aligned}\Delta G_1^\circ &= -nFE^\circ = -2 \times 23 \times 0.91 = -42.0 \text{ kcal} \\ \Delta G_2^\circ &= -nFE^\circ = -1 \times 23 \times 0.41 = -9.4 \text{ kcal} \\ \hline \Delta G_3^\circ &= -nFE^\circ = -3 \times 23 \times E_3^\circ = -51.4 \text{ kcal} \\ E_3^\circ &= 0.74 \text{ volt}\end{aligned}$$

The value n in processes 1, 2, and 3 is different. It is thus necessary for us to convert E° values to ΔG° values before addition, *since only ΔG° values are truly additive.*

For purposes of this course, all of our equations are of a type such that nF cancels and E° values are additive.

Reflection on the equation

$$\Delta G^\circ = -nFE^\circ$$

provides us with an answer to another question which frequently troubles students. Suppose we are considering the half-cell reaction $\text{Ag}^+(\text{aq}) + e^- \rightleftharpoons \text{Ag(s)}$, with an E° value of 0.80 volt. Suppose we double this equation in order to balance an overall equation [i.e., $2\text{Ag}^+(\text{aq}) + 2e^- \rightleftharpoons 2\text{Ag(s)}$]. Why don't we double the value of E° ? It is apparent that we double our value of ΔG° when we take two moles of Ag instead of one, but note that, in doing this, we also double the number of electrons being transferred, hence E° remains unchanged. That is,

$$\begin{aligned}E^\circ &= \frac{-\Delta G^\circ}{nF} = -\frac{1 \times \Delta G}{1 \times F} = -\frac{2 \times \Delta G^\circ}{2 \times F} \\ &= -\frac{3 \times \Delta G}{3 \times F}\end{aligned}$$

and so forth. Thus we see that E° is a measure of the reaction tendency, not a measure of the total energy content of the system. In many ways E° is comparable to temperature in thermal systems. If we have 100 g of water at 100°C and we add to this another 100 g of water at 100°C , the temperature of the system remains at 100°C . We don't alter the intensity factor by changing the quantity of water, but we do change the *quantity* of heat (energy) stored in the system. Neither is E° changed by doubling the size of the cell, but we do double the *quantity* of energy stored in the system. Small cells have the same voltage as big cells, but they can't produce current for as long.

THE EFFECTS OF CONCENTRATION ON E VALUES FOR A PROCESS

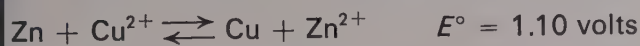
We have been careful to define E° as the voltage for a given cell when all effective concentrations are one mole/liter and all effective gas pressures are one atmosphere. We have also noticed that if we change the concentrations or gas pressures the E value for the cell changes from that of E° . It would be convenient if we could simply add to or subtract from E° a correction term to com

compensate for changes of concentration. Fortunately such a calculation is possible. By methods we prefer not to give here, we can derive a relationship which has the form

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[\text{products}]}{[\text{reactants}]}$$

the quantity subtracted being the correction term for the concentration effect. The expression involving products and reactants has the same form as the equilibrium constant.

Again consider, as an example, the equation



The value of E at some concentration other than the standard 1 M becomes

$$E = E^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

If we reduce the concentration of Zn^{2+} , the size of the second term gets smaller; we subtract a smaller number from E° , hence E is larger, as we would expect from Le Chatelier's Principle. If $[\text{Zn}^{2+}]$ and $[\text{Cu}^{2+}]$ are both 1, the second term goes to zero, and $E = E^{\circ}$, as our definition of E° demands. Finally, if Zn^{2+} and Cu^{2+} are at their equilibrium concentrations then $\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = K$ for the process, and our equation becomes

$$E = E^{\circ} - \frac{0.0591}{2} \log K = 0$$

The voltage is zero when the cell system reaches equilibrium.

The value of E is not particularly sensitive to small changes in concentration. Suppose we keep the concentration of Cu^{2+} constant at unit strength and cut the concentration of Zn^{2+} to one-tenth of its original value. We find that E then becomes

$$\begin{aligned} E &= E^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \\ &= 1.10 - \frac{0.0591}{2} \log \frac{0.1}{1} \end{aligned}$$

$$\begin{aligned} E &= 1.10 - \frac{0.0591}{2} \times -1 \\ &= 1.10 + 0.030 = 1.13 \text{ volts} \end{aligned}$$

A tenfold change in the concentration of Zn^{2+} gives a change of only 0.03 volt in the value of E .

FACTORS DETERMINING THE SIZE OF E° VALUES

Your students are undoubtedly curious at this point about the factors that make E° values large or small. The quantity E° is a measure of free energy change, and ΔG is the combination of stability change (ΔH) and randomness change ($T\Delta S$).

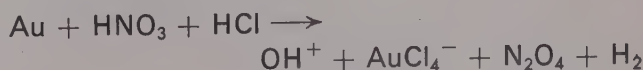
$$\Delta G = \Delta H - T\Delta S$$

Thus E° is fixed by the factors which determine relative stability (ΔH) (such as bond strengths, ionization energies, hydration energies) and by the factors which determine randomness (ΔS) (about which we have said rather little). More will be said about the factors influencing ΔH (hence, ΔG) in the Teacher's Guide for Chapter 17.

BALANCING OXIDATION-REDUCTION EQUATIONS

Three methods have been given for balancing oxidation-reduction equations. The methods simply demand that, in the end, we conserve atoms and charge. As further proof of this point, it is interesting to note that we can set up a completely algebraic process for balancing redox equations—a process based solely upon our conservation laws. Also we can use oxidation numbers as a bookkeeping device to insure conservation. An example worked by two of the various methods may be instructive.

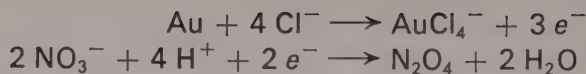
Suppose we use the example on p. 299; gold dissolving in aqua regia.



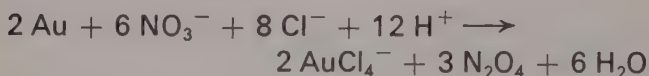
Using Half-Reactions:

The necessary half-reactions are not included in the Textbook but in a chemical handbook

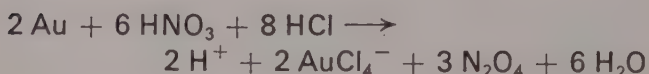
we find



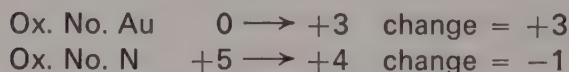
Multiply the first equation by 2 and the second by 3 and then add to get



There is no H^+ shown on the right side so we add 2H^+ to each side. That gives 14H^+ on the left, just enough to be associated with the chloride and nitrate.



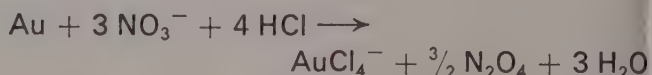
Using Oxidation Numbers:



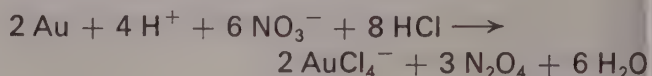
Writing just those species containing atoms whose oxidation numbers change gives



To balance chlorine atoms we add HCl to the left; to balance oxygen atoms, water is needed on the right.



Now hydrogen atoms are not balanced. Add two H^+ on the left and clear the fraction $\frac{3}{2}$.



To form HNO_3 requires 2 more H^+ on the left, so they must appear on the right. The final result is as before.

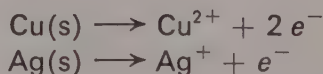
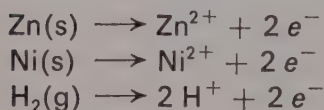
Answers to Exercises and Problems

Exercise 15-1

From the statement that nickel reacts with H^+ to give H_2 and the additional information that zinc metal reacts readily with Ni^{2+} , decide where to place the Ni-Ni^{2+} equation in our list.

Answer

The Ni-Ni^{2+} half-reaction will appear above hydrogen but below zinc. Thus



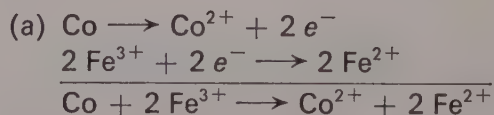
Exercise 15-2

Calculate the potential expected for the following combinations of half-reactions. Assume all ions are 1 M.

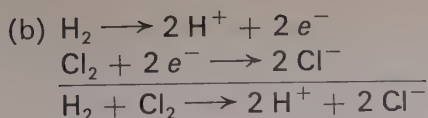
- $\text{Co} + \text{Fe}^{3+}$ gives $\text{Co}^{2+} + \text{Fe}^{2+}$
- $\text{H}_2 + \text{Cl}_2$ gives $\text{H}^+ + \text{Cl}^-$
- $\text{I}^- + \text{MnO}_4^-$ in acid solution gives $\text{I}_2 + \text{Mn}^{2+}$
- Will $\text{Ag} + \text{Cl}^-$ produce $\text{Ag}^+ + \text{Cl}_2$?

Answer: (c) +0.99 volt

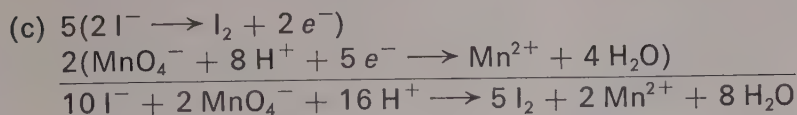
Answer to Exercise 15-2



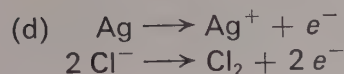
$$\begin{aligned}E^\circ &= +0.28 \text{ volt} \\ E^\circ &= +0.77 \text{ volt} \\ E^\circ_{\text{net}} &= +1.05 \text{ volts}\end{aligned}$$



$$\begin{array}{rcl}
 E^\circ & = & 0.00 \text{ volt} \\
 E^\circ & = & +1.36 \text{ volts} \\
 \hline
 E^\circ_{\text{net}} & = & +1.36 \text{ volts}
 \end{array}$$



$$\begin{array}{rcl}
 E^\circ & = & -0.53 \text{ volt} \\
 E^\circ & = & +1.52 \text{ volts} \\
 \hline
 E^\circ_{\text{net}} & = & +0.99 \text{ volt}
 \end{array}$$

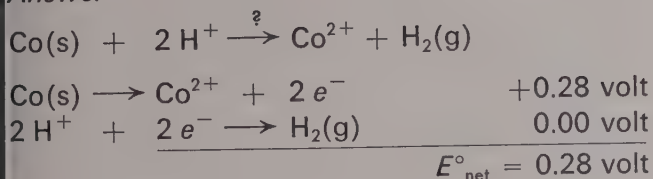


The proposed reaction will not occur to any appreciable extent. Each half-reaction produces electrons.

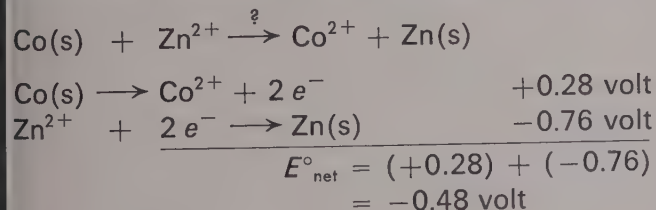
Exercise 15-3

Use E° values in Table 15-2 to predict whether cobalt metal will dissolve in 1 M HCl solution. Then predict whether cobalt metal will dissolve in 1 M zinc sulfate solution.

Answer



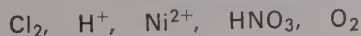
Since net E° is positive, the equilibrium state favors the products. *Cobalt will dissolve in H^+ .*



Since the net value of E° is negative, the equilibrium state favors the reactants. *Cobalt metal will not dissolve in a Zn^{2+} solution to a significant extent.*

Exercise 15-4

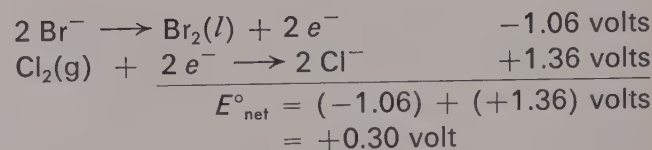
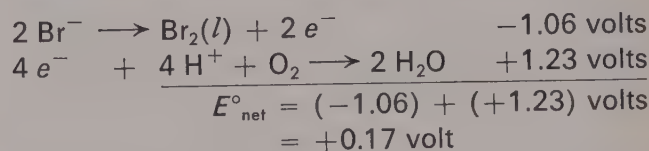
Use Table 15-2 to decide which substances in the following list tend to oxidize bromide ion, Br^- .



Answer

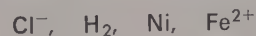
To oxidize bromide ion, it is necessary to use a half-reaction in which electrons are lost less readily than in the reaction $2 \text{Br}^- \rightleftharpoons \text{Br}_2(l) + 2 e^-$.

$2 e^-$. This is the same as saying that, to oxidize Br^- , electrons must be removed by another half-reaction. To accomplish this, we need a half-reaction whose E° is less than -1.06 volts. In the list of choices, only O_2 and Cl_2 half-reactions have an E° less than -1.06 volts.



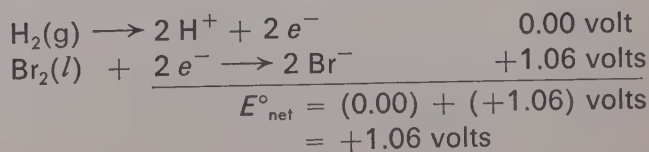
Exercise 15-5

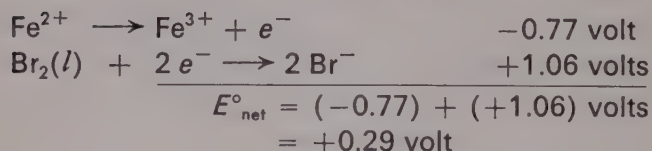
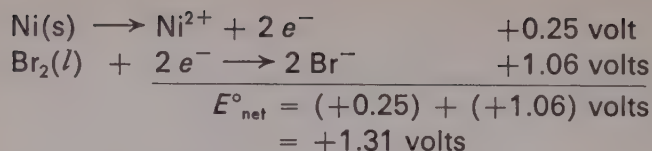
Use Table 15-2 to decide which substances in the following list tend to reduce bromine, Br_2 .



Answer

To reduce $\text{Br}_2(l)$ it is necessary to use a half-reaction in which electrons are lost more readily than in the reaction $2 \text{Br}^- \rightleftharpoons \text{Br}_2(l) + 2 e^-$. To do this, we need a half-reaction whose E° is greater (more positive) than -1.06 volts. In the list of choices, $\text{H}_2(\text{g})$, Fe^{2+} , and Ni(s) half-reactions satisfy the requirement.

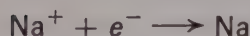


**Exercise 15-6**

The electrolysis of fused NaCl produces sodium metal at the cathode and chlorine gas at the anode. Write equations for the two half-reactions that occur in this electrolysis.

Answer

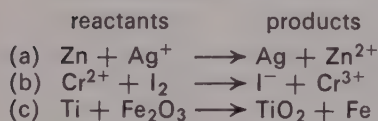
at the cathode



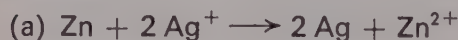
at the anode

**Exercise 15-7**

Write balanced equations for these redox reactions by inspection.



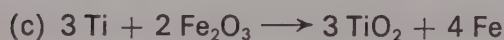
Answer



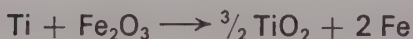
The clue is the different charges on the silver and zinc ions.



Start by balancing iodine, then balance charges.



Start by balancing oxygen and iron



Then balance Ti



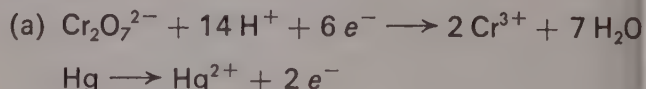
The equation is balanced. Multiplying by 2 gives the equation first listed.

Exercise 15-8

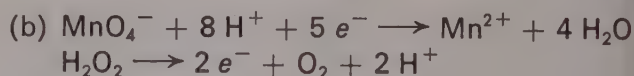
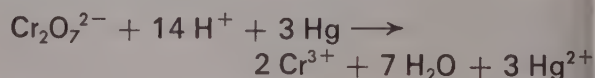
Write balanced equations for these reactions by finding the half-reaction equations in Appendix 4.

- (a) $\text{Cr}_2\text{O}_7^{2-} + \text{Hg} \longrightarrow \text{Cr}^{3+} + \text{Hg}^{2+}$
 (b) $\text{MnO}_4^{-} + \text{H}_2\text{O}_2 \longrightarrow \text{Mn}^{2+} + \text{O}_2$
 (c) $\text{H}_2\text{O}_2 + \text{SO}_2 \longrightarrow \text{H}_2\text{O} + \text{SO}_4^{2-}$

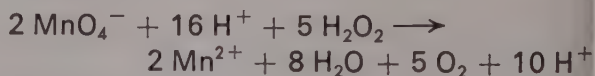
Answer



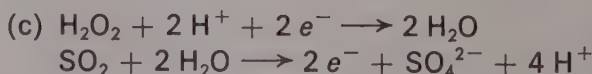
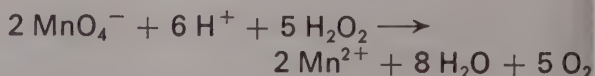
Multiply the second equation by 3 and add.



Multiply the first equation by 2, the second by 5, and add.



Subtract 10 H⁺ from each side



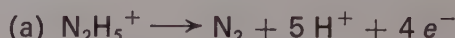
Adding gives

**Exercise 15-9**

Write balanced equations for these redox reactions using Method III.

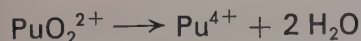
- (a) $\text{N}_2\text{H}_5^{+} + \text{PuO}_2^{2+} \longrightarrow \text{Pu}^{4+} + \text{N}_2$
 (b) $\text{Zn} + \text{NO}_3^{-} \longrightarrow \text{NH}_4^{+} + \text{Zn}^{2+}$
 (c) $\text{S}_2\text{O}_6^{2-} + \text{BiO}_3^{-} \longrightarrow \text{Bi}^{3+} + \text{SO}_4^{2-}$

Answer



only steps 3 and 4 are needed for this half-reaction

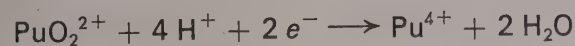
For the second one, first balance oxygen



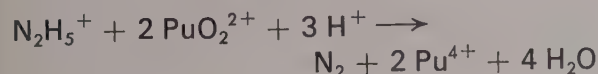
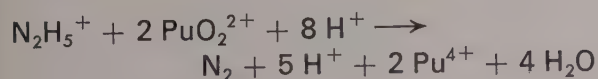
then hydrogen



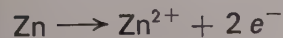
then charge



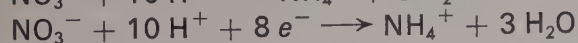
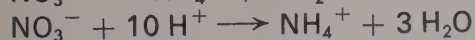
Now combine by doubling the second half-reaction so electrons cancel.



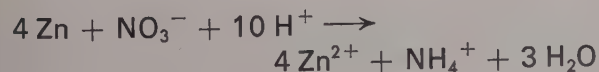
(b) The zinc half-reaction is in Appendix 4.



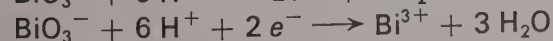
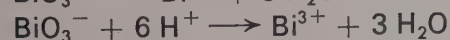
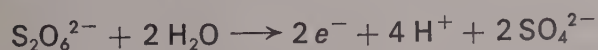
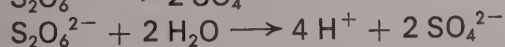
Following the steps above gives



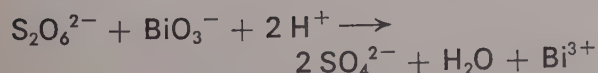
Multiply the zinc half-reaction by 4 and add to cancel electrons



(c) $\text{S}_2\text{O}_6^{2-} \longrightarrow 2 \text{SO}_4^{2-}$

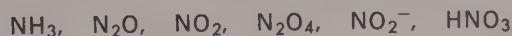


Combining



Exercise 15-10

Nitrogen forms a large number of compounds with hydrogen and oxygen. Calculate the oxidation numbers for N in these compounds.



Answer

All numbers are oxidation numbers

NH_3	H is +1	so N is -3
N_2O	O is -2	so N is +1
NO_2	O is -2	so N is +4
N_2O_4	O is -2	so N is +4
NO_2^-	O is -2	so N is +3
HNO_3	O is -2, H is +1	so N is +5

Exercise 15-11

Calculate the oxidation numbers for the P in these acids.



Answer

All numbers are oxidation numbers. In each acid H is +1 and oxygen -2.

$$\text{H}_3\text{PO}_2 \quad 3(+1) + (\text{Ox. No. P}) + 2(-2) = 0$$

$$\text{Ox. No. P} = 4 - 3 = +1$$

$$\text{H}_3\text{PO}_3 \quad 3(+1) + (\text{Ox. No. P}) + 3(-2) = 0$$

$$\text{Ox. No. P} = 6 - 3 = +3$$

$$\text{H}_3\text{PO}_4 \quad 3(+1) + (\text{Ox. No. P}) + 4(-2) = 0$$

$$\text{Ox. No. P} = 8 - 3 = +5$$

Problem 1

- (a) If a neutral atom becomes positively charged, has it been oxidized or reduced? Write a general equation using M for the neutral atom.
- (b) If an ion X^- acquires a 2- charge, has it been oxidized or reduced? Write a general equation.

Answer

(a) Oxidized; $\text{M} \longrightarrow \text{M}^+ + e^-$

The atom M has lost an electron; thus it has undergone one type of oxidation.

(b) Reduced; $\text{X}^- + e^- \longrightarrow \text{X}^{2-}$

The ion X^- gained an electron which constitutes one type of reduction.

There are a number of other types. Those above are clear-cut cases of electron loss or gain. Later, cases will be considered in

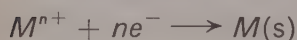
which it is not clear whether there has been an electron transfer (e.g., when NO changes to NO₂). A change in oxidation number of N has occurred.

Problem 2

If you wish to replate a silver spoon, would you make it the anode or cathode in a cell? Use half-reactions in your explanation. How many moles of electrons are needed to plate out 1.0 gram of Ag?

Answer

To plate out any metal, positive metallic ions must be changed to neutral atoms:



Such a reaction involves reduction. Since reduction takes place at the cathode, the spoon to be plated should be made the cathode.

For this case, the cathode reaction (reduction) would be



To determine moles of electrons needed to plate out 1.0 gram of Ag(s):

g Ag/molar mass Ag

$$1.0 \text{ g} / (108 \text{ g/mole}) = \frac{1.0}{108} \text{ mole of Ag}$$

$$\text{mole Ag} \times \frac{\text{mole } e^{-}}{\text{mole Ag}} = \text{mole } e^{-}$$

$$\frac{1.0}{108} \times \frac{1}{1} = 0.0093 \text{ mole of electrons}$$

Problem 3

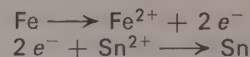
Figure 15-2 shows electrons leaving the Cu(s) electrode and going to the Ag(s) electrode. Experimentally, both half-cells are found to be electrically neutral before current flows and to remain so as the cell operates. Explain this.

Answer

The half-cells remain electrically neutral (equal number of positive and negative charges) by movement of ions. As more Cu²⁺ ions are made, nitrate ions move into the copper half-cell. At the same time, Ag⁺ ions are being removed, hence there is no excessive positive charge left in the silver half-cell.

Problem 4

Equations for two half-reactions taking place in an electrochemical cell are:



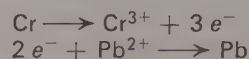
Which metal serves as the anode? Which the cathode?

Answer

Oxidation occurs at the anode; Fe is the anode. Reduction takes place at the cathode; Sn is the cathode.

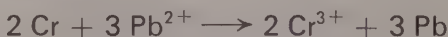
Problem 5

Equations for two half-reactions taking place in an electrochemical cell are:



This cell is similar to the one discussed in Section 15-1, page 278. How many grams of Pb will deposit on the cathode when 1.56 grams of Cr dissolves from the anode?

Answer



$$1.56 \text{ g Cr is } \frac{1.56 \text{ g}}{52 \text{ g/mole}} = 0.030 \text{ mole}$$

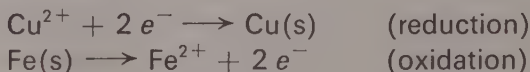
For each two moles of chromium dissolving, three moles of lead deposit. Each mole of lead contains 207 g.

$$0.030 \times \frac{3}{2} \times 207 = 9.3 \text{ g Pb deposited}$$

Problem 6

One method of obtaining copper metal is to let a solution containing Cu²⁺ ions trickle over scrap iron. Write the equations for the two half-reactions. Assume Fe²⁺ forms. Indicate in which half-reaction oxidation is taking place.

Answer

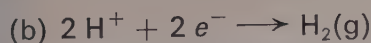


Problem 7

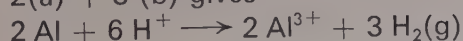
Aluminum metal reacts with acidic solutions to liberate hydrogen gas. Write equations for the two half-reactions and the net ionic reaction.

Answer

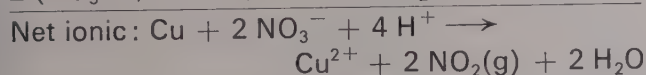
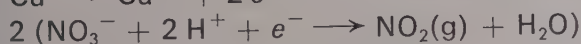
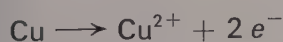




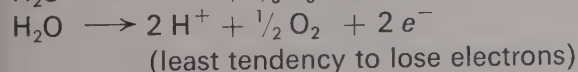
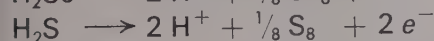
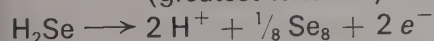
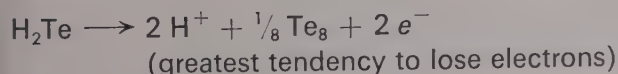
2(a) + 3 (b) gives

**Problem 8**

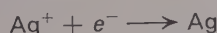
When copper is placed in concentrated nitric acid, vigorous bubbling takes place as a brown gas is evolved. The copper disappears and the solution changes from colorless to a greenish-blue. The brown gas is nitrogen dioxide, NO_2 , and the solution's color is due to the formation of cupric ion, Cu^{2+} . Using half-reactions from Appendix 4, write the net equation for this reaction.

Answer**Problem 9**

In acid solution the following are true: H_2S will react with oxygen to give H_2O and sulfur. H_2S will not react in the corresponding reaction with selenium or tellurium. H_2Se will react with sulfur giving H_2S and selenium but it will not react with tellurium. Arrange the hydrides of column VI, H_2O , H_2S , H_2Se , and H_2Te , in order of their tendency to lose electrons to form the elements, O_2 , S_8 , Se_8 , and Te_8 .

Answer**Problem 10**

How many coulombs are needed to form 1 mole of Ag from a 1 M $AgNO_3$ solution?

*Answer*

9.6×10^4 coulombs needed.

Problem 11

A 100 watt light bulb, when operated in a 110 volt household circuit, has a current of 0.9 ampere flowing through it. In one minute, how many electrons pass through the light bulb?

Answer

$$(0.9 \text{ amp}) \left(\frac{60 \text{ sec}}{1 \text{ min}} \right) \left(\frac{1 \text{ mole electrons}}{9.6 \times 10^4 \text{ coulombs}} \right) \times$$

$$\left(6.0 \times 10^{23} \frac{\text{electrons}}{\text{mole}} \right) = 4 \times 10^{20} \text{ electrons/min}$$

Problem 12

A flashlight bulb will burn out almost instantly if connected to a 110 volt household circuit. This does not happen if a $1\frac{1}{2}$ volt dry cell is connected to the bulb. Explain.

Answer

The filament of the bulb has a certain resistance. A high voltage will cause a larger current to flow than a low voltage will. The higher current produces a high temperature which melts the filament.

Problem 13

If a copper wire carries a 0.1 ampere current, how many moles of electrons pass through the wire each second?

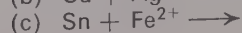
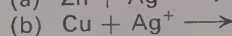
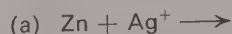
Answer

$$(0.1 \text{ amp}) \left(\frac{1 \text{ sec}}{\text{sec}} \right) \left(\frac{1 \text{ mole}}{9.6 \times 10^4 \text{ coulombs}} \right)$$

$$= 10^{-6} \text{ mole of electrons pass in 1 second}$$

Problem 14

Complete the following equations. Determine the net voltage of each cell and decide whether reaction can occur.



Answer

	E°
(a) $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2 e^-$	0.76 volt
$2(\text{Ag}^+ + e^- \longrightarrow \text{Ag})$	+0.80 volt
$\text{Zn} + 2 \text{Ag}^+ \rightleftharpoons \text{Zn}^{2+} + 2 \text{Ag}$	$E^\circ_{\text{net}} = 1.56 \text{ volts}$
Equilibrium favors products.	
(b) $\text{Cu} \longrightarrow \text{Cu}^{2+} + 2 e^-$	-0.34 volt
$2(\text{Ag}^+ + e^- \longrightarrow \text{Ag})$	+0.80 volt
$\text{Cu} + 2 \text{Ag}^+ \rightleftharpoons \text{Cu}^{2+} + 2 \text{Ag}$	$E^\circ_{\text{net}} = 0.46 \text{ volt}$
Equilibrium favors products.	
(c) $\text{Sn} \longrightarrow \text{Sn}^{2+} + 2 e^-$	0.14 volt
$\text{Fe}^{2+} + 2 e^- \longrightarrow \text{Fe}$	-0.44 volt
$\text{Sn} + \text{Fe}^{2+} \rightleftharpoons \text{Sn}^{2+} + \text{Fe}$	$E^\circ_{\text{net}} = -0.30 \text{ volt}$
Equilibrium favors reactants.	
(d) $\text{Hg} \longrightarrow \text{Hg}^{2+} + 2 e^-$	-0.78 volt
$2 \text{H}^+ + 2 e^- \longrightarrow \text{H}_2$	0.00 volt
$\text{Hg} + 2 \text{H}^+ \rightleftharpoons \text{Hg}^{2+} + \text{H}_2$	$E^\circ_{\text{net}} = -0.78 \text{ volt}$
Equilibrium favors reactants.	

Problem 15

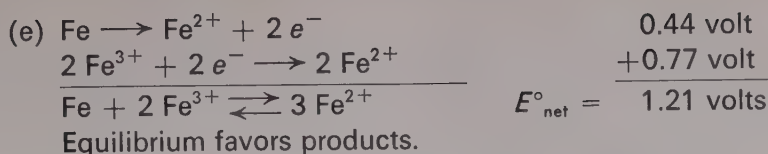
For each of the following,

- write the equations for the half-reactions;
- determine the net equation;
- predict whether the reaction can occur, giving the basis for your prediction:

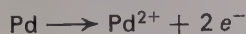
- $\text{Mg(s)} + \text{Sn}^{2+} \longrightarrow$
- $\text{Mn(s)} + \text{Cs}^+ \longrightarrow$
- $\text{Cu(s)} + \text{Cl}_2(\text{g}) \longrightarrow$
- $\text{Zn(s)} + \text{Fe}^{2+} \longrightarrow$
- $\text{Fe(s)} + \text{Fe}^{3+} \longrightarrow$

Answer

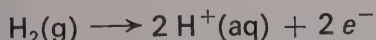
(a) $\text{Mg} \longrightarrow \text{Mg}^{2+} + 2 e^-$	2.37 volts
$\text{Sn}^{2+} + 2 e^- \longrightarrow \text{Sn}$	-0.14 volt
$\text{Mg} + \text{Sn}^{2+} \rightleftharpoons \text{Mg}^{2+} + \text{Sn}$	$E^\circ_{\text{net}} = 2.23 \text{ volts}$
Equilibrium favors products.	
(b) $\text{Mn} \longrightarrow \text{Mn}^{2+} + 2 e^-$	1.18 volts
$2 \text{Cs}^+ + 2 e^- \longrightarrow 2 \text{Cs}$	-2.92 volts
$\text{Mn} + 2 \text{Cs}^+ \rightleftharpoons \text{Mn}^{2+} + 2 \text{Cs}$	$E^\circ_{\text{net}} = -1.74 \text{ volts}$
Equilibrium favors reactants.	
(c) $\text{Cu} \longrightarrow \text{Cu}^{2+} + 2 e^-$	-0.34 volt
$\text{Cl}_2 + 2 e^- \longrightarrow 2 \text{Cl}^-$	+1.36 volts
$\text{Cu} + \text{Cl}_2 \rightleftharpoons \text{Cu}^{2+} + 2 \text{Cl}^-$	$E^\circ_{\text{net}} = 1.02 \text{ volts}$
Equilibrium favors products.	
(d) $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2 e^-$	0.76 volt
$\text{Fe}^{2+} + 2 e^- \longrightarrow \text{Fe}$	-0.44 volt
$\text{Zn} + \text{Fe}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Fe}$	$E^\circ_{\text{net}} = 0.32 \text{ volt}$
Equilibrium favors products.	

**Problem 16**

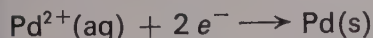
A half-cell consisting of a palladium rod dipping into a 1 M $\text{Pd}(\text{NO}_3)_2$ solution is connected with a standard hydrogen half-cell. The cell voltage is 0.99 volt and the platinum electrode in the hydrogen half-cell is the anode. Determine E° for the reaction

**Answer**

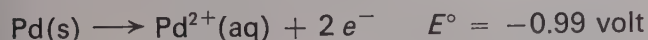
Oxidation occurs at the anode, which is given as the hydrogen electrode. The anode reaction must be



These liberated electrons must be used at the cathode by the reaction



Since the cell voltage is given as +0.99 volt, we have by reversing the equation

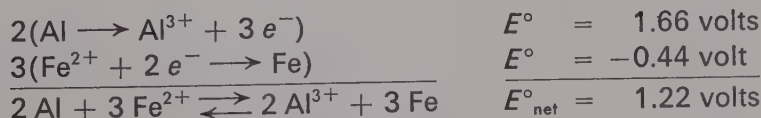
**Problem 17**

Suppose chemists had chosen the reference reaction to be $2\text{I}^- \longrightarrow \text{I}_2 + 2e^-$ with zero potential.

- (a) What would E° have been for $\text{Na} \longrightarrow \text{Na}^+ + e^-$?
 (b) How much would the net potential have been changed for the reaction

**Problem 19**

What will happen if an aluminum spoon is used to stir

Answer

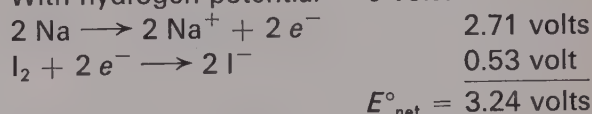
The aluminum spoon would dissolve. Nothing would happen to the iron spoon. The reverse reaction does not occur to a significant extent.

Answer to Problem 17

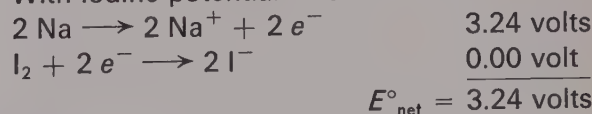
- (a) $\text{Na} \longrightarrow \text{Na}^+ + e^-$ would be 0.53 volt more positive, or $E^\circ = 2.71 + 0.53 = 3.24$ volts. All other half-cells would also be 0.53 volt more positive.

- (b) No change.

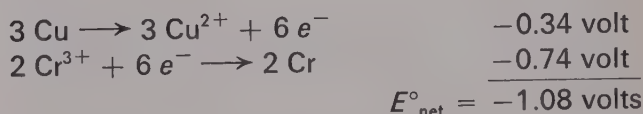
With hydrogen potential = 0 volt:



With iodine potential = 0 volt:

**Problem 18**

If a piece of copper metal is dipped into a solution containing Cr^{3+} ions, what will happen? Explain, using E° values.

Answer:

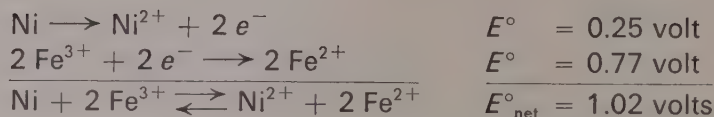
Practically no reaction occurs spontaneously. We might use $\text{Cu} \longrightarrow \text{Cu}^+ + e^-$, but this is even more negative (-0.52 volt), and E°_{net} is then -1.26 volts.

an $\text{Fe}(\text{NO}_3)_2$ solution? What will happen if an iron spoon is used to stir an AlCl_3 solution?

Problem 20

Can 1 M $\text{Fe}_2(\text{SO}_4)_3$ solution be stored in a container made of nickel metal? Explain your answer.

Answer



No. The container would dissolve.

Since E°_{net} is positive, the reaction dissolving nickel occurs spontaneously.

Problem 21

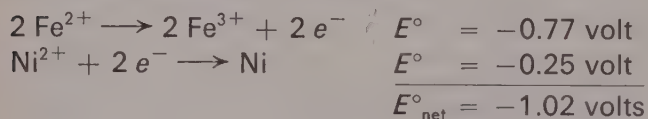
In Section 15-6, the reaction of iron with a solution of nickel ions was discussed. Will the reaction



occur? What is the net voltage?

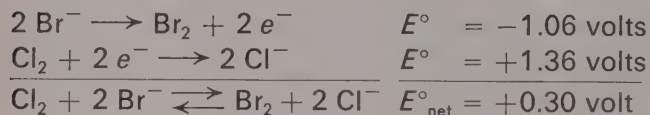
Answer

No. Net voltage is -1.02 volts.

**Problem 22**

Most of the bromine produced in the United States is made by oxidizing Br^- to Br_2 using Cl_2 . What is E° for this reaction?

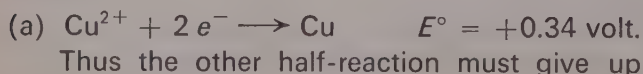
Answer

**Problem 23**

Which of the half-reactions will spontaneously reduce Cu^{2+} to Cu(s) ?

- Sn^{2+} to Sn^{4+}
- Cl^- to $\text{Cl}_2(\text{g})$
- Au to Au^{3+}
- MnO_4^- to Mn^{2+}
- Ag to Ag^+

Answer



electrons and be positive or no more negative than -0.34 . Reaction (a) is the only one that satisfies both conditions.

Problem 24

Which of the half-reactions will spontaneously oxidize Fe^{2+} to Fe^{3+} ?

- Ag^+ to Ag
- Pb^{2+} to Pb
- Al^{3+} to Al
- MnO_4^- to Mn^{2+}
- Li to Li^+

Answer

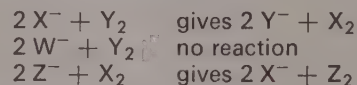
- (a) and (d)



Thus the other half-reaction must use up electrons and be positive by 0.77 volt or more.

Problem 25

The four elements W, X, Y, and Z form diatomic molecules and also form singly charged negative ions. The following observations are made in a series of experiments.



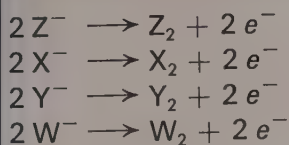
Use these observations to write equations for each oxidation half-reaction. Arrange them in a short oxidation potential series. Which ion is the strongest reducing agent? Which molecule is the strongest oxidizing agent?

Answer

Clearly X^- can reduce Y_2 and Z^- can reduce X_2 . Since W^- cannot reduce Y_2 , we can list Z^- as the most powerful reducing agent and W_2 as the

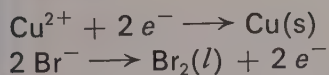
ANSWERS TO EXERCISES AND PROBLEMS

strongest oxidizing agent. The resulting list is

**Problem 26**

In the electrolysis of aqueous cupric bromide, CuBr_2 , 0.500 gram of copper is deposited at one electrode. How many grams of bromine are formed at the other electrode? Write the anode and cathode half-reactions.

Answer



$$\begin{aligned} \text{Step I: } 0.500 \text{ g Cu is } \frac{0.500 \text{ g}}{63.5 \text{ g/mole}} \\ = 7.87 \times 10^{-3} \text{ mole Cu} \end{aligned}$$

Step II: One mole of Br_2 is formed for every mole of Cu. Therefore 7.87×10^{-3} mole of Br_2 is formed with 7.87×10^{-3} mole of Cu.

Step III: 7.87×10^{-3} mole gives 7.87×10^{-3} mole $\times 159.8 \text{ g/mole} = 1.26 \text{ g Br}_2(l)$

Problem 27

Determine the oxidation number of uranium in each of

these known compounds: UO_3 , U_3O_8 , U_2O_5 , UO_2 , UO , K_2UO_4 , MgU_2O_7 .

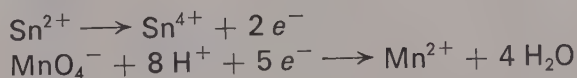
Answer to Problem 27

	Ox. No.	Ox. No.
UO_3	$3 \text{ O} = -6$	$\text{U} = +6$
U_3O_8	$8 \text{ O} = -16$	$\text{U} = +(\frac{16}{3})$
U_2O_5	$5 \text{ O} = -10$	$\text{U} = +5$
UO_2	$2 \text{ O} = -4$	$\text{U} = +4$
UO	$\text{O} = -2$	$\text{U} = +2$
K_2UO_4	$4 \text{ O} = -8$	
	$2 \text{ K} = +2$	$\text{U} = +6$
	$\hline -6$	
MgU_2O_7	$7 \text{ O} = -14$	
	$\text{Mg} = +2$	$\text{U} = +6$
	$\hline -12$	

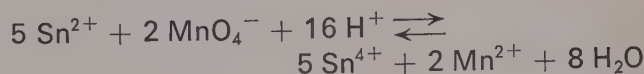
Problem 28

Write a balanced equation for the reaction between stannous ion, Sn^{2+} , and permanganate ion, MnO_4^- , in acid solution to produce stannic ion, Sn^{4+} , and manganous ion, Mn^{2+} .

Answer



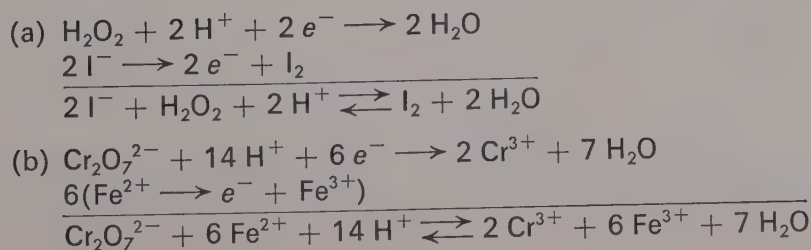
Multiply the first equation by 5, the second by 2, and add.

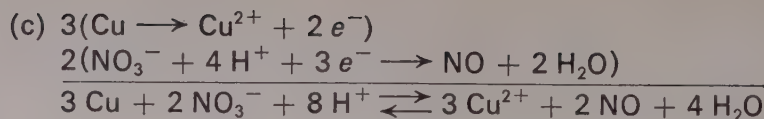
**Problem 29**

Use Appendix 4 to write a balanced equation for each of the following reactions:

- (a) $\text{H}_2\text{O}_2 + \text{I}^- + \text{H}^+$ gives $\text{H}_2\text{O} + \text{I}_2$
 (b) $\text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{2+} + \text{H}^+$ gives $\text{Cr}^{3+} + \text{Fe}^{3+} + \text{H}_2\text{O}$
 (c) $\text{Cu} + \text{NO}_3^- + \text{H}^+$ gives $\text{Cu}^{2+} + \text{NO} + \text{H}_2\text{O}$

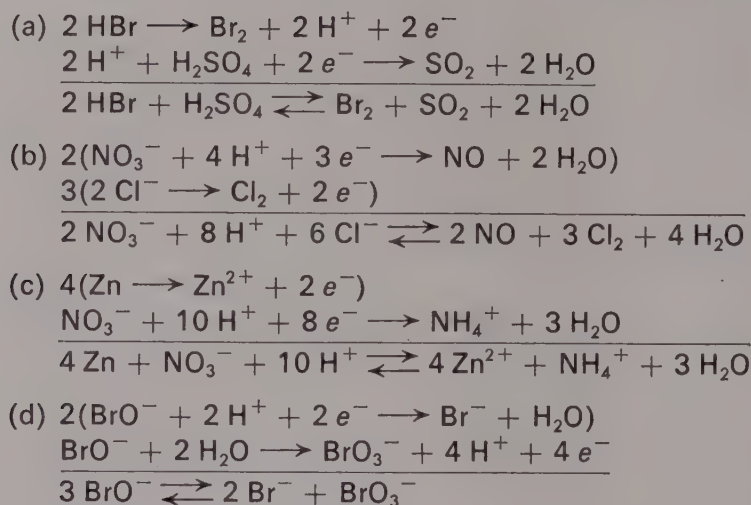
Answer



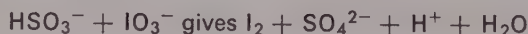
**Problem 30**

Give a balanced equation for each of the following reactions:

- (a) $\text{HBr} + \text{H}_2\text{SO}_4$ gives $\text{SO}_2 + \text{Br}_2 + \text{H}_2\text{O}$
 (b) $\text{NO}_3^- + \text{Cl}^- + \text{H}^+$ gives $\text{NO} + \text{Cl}_2 + \text{H}_2\text{O}$
 (c) $\text{Zn} + \text{NO}_3^- + \text{H}^+$ gives $\text{Zn}^{2+} + \text{NH}_4^+ + \text{H}_2\text{O}$
 (d) BrO^- gives $\text{Br}^- + \text{BrO}_3^-$

Answer**Problem 31**

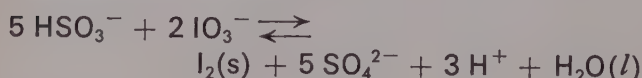
Iodine is recovered from iodates in Chile saltpeter by the reaction



- (a) How many grams of sodium iodate, NaIO_3 , react with 1.00 mole of KHSO_3 ?
 (b) How many grams of iodine, I_2 , are produced?

Answer

The balanced equation is



(a) Step I

Given 1.00 mole of HSO_3^- .

Step II

$$(\text{moles } \text{HSO}_3^-) \left(\frac{\text{moles } \text{IO}_3^-}{\text{mole } \text{HSO}_3^-} \right) = \text{moles } \text{IO}_3^-$$

$$1.00 \times \frac{2}{5} = 0.400 \text{ mole } \text{IO}_3^-$$

0.400 mole IO_3^- is obtained from 0.400 mole NaIO_3 .

Step III

$$\begin{aligned}
 &(\text{mole } \text{NaIO}_3)(\text{g } \text{NaIO}_3/\text{mole}) \\
 &= 0.400 \times 198 = 79.2 \text{ g } \text{NaIO}_3
 \end{aligned}$$

(b) Step I

Given 1.00 mole KHSO_3 .

Step II

$$(\text{moles } \text{KHSO}_3) \left(\frac{\text{moles } \text{I}_2}{\text{mole } \text{KHSO}_3} \right) = \text{moles } \text{I}_2$$

$$1.00 \times \frac{1}{5} = 0.200 \text{ mole } \text{I}_2$$

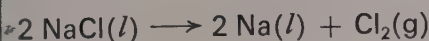
Step III

$$\begin{aligned}
 &(\text{moles } \text{I}_2)(\text{g } \text{I}_2/\text{mole}) = \text{g } \text{I}_2 \\
 &0.200 \times 254 = 50.8 \text{ g } \text{I}_2 \text{ produced}
 \end{aligned}$$

Problem 32

The chlorine used to purify your drinking water was probably made by electrolyzing molten NaCl to produce liquid sodium and gaseous chlorine.

- (a) How many grams of sodium chloride are needed to produce 355 grams of chlorine gas?
 (b) What volume would this gas occupy at STP?

Answer**(a) Step I**

$$\begin{aligned} \text{g Cl}_2 / \text{g Cl}_2 / \text{mole} &= \text{moles Cl}_2 \\ 355 / 71.0 &= 5.00 \text{ moles Cl}_2 \end{aligned}$$

Step II

$$(\text{moles Cl}_2) \left(\frac{\text{moles NaCl}}{\text{mole Cl}_2} \right) = \text{moles NaCl}$$

$$5.00 \times \frac{2}{1} = 10.0 \text{ moles NaCl}$$

Step III

$$\begin{aligned} (\text{moles NaCl})(\text{g NaCl/mole}) &= \text{grams NaCl} \\ 10.0 \times 58.5 &= 585 \text{ g NaCl needed} \end{aligned}$$

- (b) To find the volume occupied at STP:

$$\begin{aligned} (\text{moles Cl}_2) \left[\frac{\text{liters Cl}_2 (\text{STP})}{\text{mole Cl}_2} \right] \\ = \text{liters Cl}_2 (\text{STP}) \end{aligned}$$

$$5.00 \times \frac{22.4}{1} = 112 = 1.12 \times 10^2 \text{ liters}$$

Problem 33

A 6 volt lead storage battery contains 700 grams of pure $\text{H}_2\text{SO}_4(l)$ dissolved in water.

- (a) How many grams of solid sodium carbonate, Na_2CO_3 , would be needed to neutralize this acid (giving CO_2 gas and H_2O) if it were spilled?
 (b) How many liters of 2.0 M Na_2CO_3 solution would be needed?

Answer**(a) Step I**

$$\begin{aligned} \text{moles H}_2\text{SO}_4 &= (\text{g H}_2\text{SO}_4) / (\text{g H}_2\text{SO}_4 / \text{mole}) \\ &= 700 / 98.1 \text{ moles} = 7.14 \text{ moles} \end{aligned}$$

Step II

$$\begin{aligned} \text{moles H}^+ &= (\text{moles H}_2\text{SO}_4) \left(\frac{\text{moles H}^+}{\text{mole H}_2\text{SO}_4} \right) \\ &= 7.14 \times \frac{2}{1} \text{ moles} = 14.3 \text{ moles} \\ \text{moles CO}_3^{2-} &= (\text{moles H}^+) \left(\frac{\text{moles CO}_3^{2-}}{\text{mole H}^+} \right) \\ &= 14.3 \times \frac{1}{2} \text{ moles} = 7.14 \text{ moles} \end{aligned}$$

Step III

$$\begin{aligned} \text{g Na}_2\text{CO}_3 &= (\text{moles Na}_2\text{CO}_3)(\text{g Na}_2\text{CO}_3 / \text{mole}) \\ &= 7.14 \times 106 \text{ g} = 757 \text{ g} \end{aligned}$$

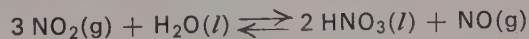
- (b) Steps I and II are the same as in (a).

Step III

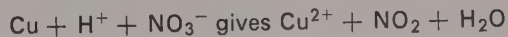
$$\begin{aligned} \text{vol 2.0 M Na}_2\text{CO}_3 \\ &= \left(\frac{\text{moles Na}_2\text{CO}_3 \text{ needed}}{\text{molar conc. Na}_2\text{CO}_3 \text{ solution}} \right) \\ \text{vol Na}_2\text{CO}_3 &= \left(\frac{7.14 \text{ moles}}{2.0 \text{ moles/liter}} \right) = 3.57 \text{ liters} \end{aligned}$$

Problem 34

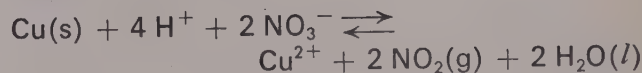
Nitric acid, HNO_3 , is made by the process



Commercial concentrated acid contains 68% by weight HNO_3 in water. The solution is 15 M. How many liters of concentrated acid are needed to react with 0.100 kg of copper metal?



Answer: 0.42 liter of HNO_3

Answer**Step I**

$$\begin{aligned} \text{moles Cu} &= \text{g Cu} / \text{g Cu/mole} \\ 100 / 63.5 &= 1.57 \text{ moles Cu} \end{aligned}$$

Step II

$$(\text{moles Cu}) \left(\frac{\text{moles H}^+}{\text{mole Cu}} \right) = \text{moles H}^+$$

$$1.57 \times \frac{4}{1} = 6.28 \text{ moles H}^+$$

$$(\text{moles H}^+) \left(\frac{\text{moles HNO}_3}{\text{mole H}^+} \right)$$

$$6.28 \times \frac{1}{1} = 6.28 \text{ moles HNO}_3$$

Step III

$$\frac{\text{moles HNO}_3}{\text{moles/liter}} = \text{liter HNO}_3$$

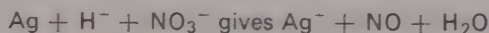
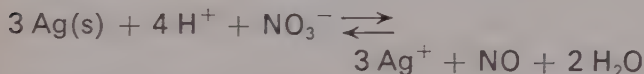
$$6.28/15 = 0.419 \text{ liter}$$

or

$$0.42 \text{ liter HNO}_3$$

Problem 35

How many grams of silver metal will react with 2.0 liters of 6.0 *M* HNO₃? The reactants and products are

*Answer*

Step I

$$\begin{aligned} \text{moles HNO}_3 &= (\text{vol HNO}_3)(\text{molar conc. HNO}_3) \\ &= (\text{liters})(\text{moles/liter}) \\ &= 2.0 \times 6.0 = 12 \text{ moles HNO}_3 \end{aligned}$$

Step II

$$(\text{moles HNO}_3) \left(\frac{\text{moles Ag}}{\text{mole HNO}_3} \right) = \text{moles Ag}$$

$$12 \times \frac{3}{4} = 9.0 \text{ moles Ag}$$

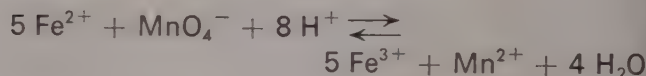
Step III

$$\text{moles Ag} \times \frac{\text{g}}{\text{mole}} = \text{grams Ag}$$

$$9.0 \times 108 = 9.7 \times 10^2 \text{ g Ag}$$

Problem 36

How many milliliters of a 0.050 *M* KMnO₄ solution are required to oxidize 2.00 grams of FeSO₄ in a dilute acid solution?

Answer: 53 ml of KMnO₄ solution*Answer*

Step I

$$\text{moles FeSO}_4 = \text{g FeSO}_4 / \text{g FeSO}_4 / \text{mole}$$

$$\frac{2.00 \text{ g}}{152 \text{ g/mole}} = 0.0132 \text{ mole FeSO}_4$$

Step II

$$\begin{aligned} (\text{moles FeSO}_4) \left(\frac{\text{moles MnO}_4^-}{\text{mole FeSO}_4} \right) \\ = \text{moles MnO}_4^- \text{ needed} \end{aligned}$$

$$1.32 \times 10^{-2} \times \frac{1}{5} = 0.264 \times 10^{-2} \text{ mole MnO}_4^-$$

Step III

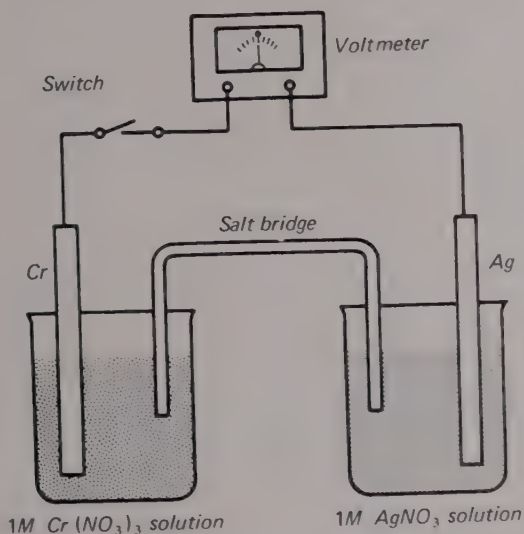
$$\begin{aligned} \left(\frac{\text{vol MnO}_4^-}{\text{solution}} \right) &= \left(\frac{\text{moles MnO}_4^- \text{ needed}}{\text{molar conc. MnO}_4^-} \right) \\ &= \frac{0.264 \times 10^{-2} \text{ mole}}{0.050 \text{ mole/liter}} \\ &= 5.3 \times 10^{-2} \text{ liter} \\ &= (5.3 \times 10^{-2} \text{ liter}) \end{aligned}$$

$$\times 1000 \text{ ml/liter} = 53 \text{ ml}$$

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

Questions 1–9 apply to the following experiment: In order to make a simple cell, a student places a strip of chromium into a beaker containing 1 M $\text{Cr}(\text{NO}_3)_3$ solution. Into another beaker, containing 1 M AgNO_3 solution, he places a strip of silver. The electrodes are connected as shown in the circuit diagram. A salt bridge is used to connect the solutions in the two beakers.



1. When the switch is closed, oxidation will occur at the (Ag, Cr) _____ electrode.

Answer: Cr.

2. Electrons flow in the external circuit (wires and voltmeter) from the (Ag, Cr) _____ electrode to the (Ag, Cr) _____ electrode.

Answer: Cr to Ag electrode.

3. (a) The (Ag, Cr) _____ electrode is the cathode.
(b) Positive ions in the solution will migrate toward the (cathode, anode) _____.

Answer

- (a) Ag.
(b) Cathode.

4. After the cell has been operating for some time, which electrode will show an increase in mass? (Ag, Cr) _____.

Answer: Ag.

5. If one mole of electrons is allowed to pass through the circuit, how many moles change will this produce at the Ag electrode? How many grams change will be produced at the Cr electrode (Ag, 107.9; Cr, 52.0)?

Answer

One mole will be added to the Ag electrode; 17.3 grams will be lost from the Cr electrode.

6. What is the maximum voltage possible for this cell?

Answer: 1.54 volts.

7. When equilibrium is established the voltage (a) increases to maximum, (b) drops to zero, (c) does not change.

Answer: (b) Drops to zero.

8. If the salt bridge is removed the voltage (a) increases to maximum, (b) drops to zero, (c) does not change.

Answer: (b) Drops to zero.

9. If 50 ml of 2 M sodium sulfide, Na_2S , were added to the half-cell containing Ag^+ ions to precipitate Ag_2S , the voltage would (a) increase, (b) decrease, (c) remain the same.

Answer: (b) Decrease.

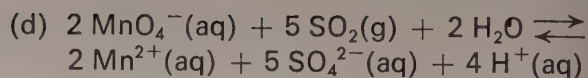
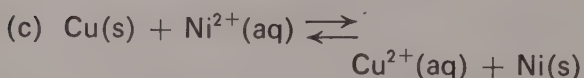
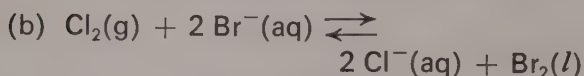
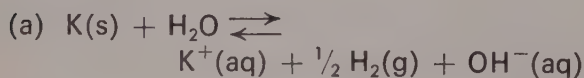
Questions 10–12 refer to the following equations:

- (a) $\text{K(s)} + \text{H}_2\text{O (distilled water)}$
(b) $\text{Cl}_2\text{(g)} + \text{Br}^-\text{(aq)}$

- (c) $\text{Cu(s)} + \text{Ni}^{2+}(\text{aq})$ [remember that Cu goes to $\text{Cu}^{2+}(\text{aq})$]
 (d) $\text{SO}_2(\text{g}) + \text{MnO}_4^{-}(\text{aq})$ in acid solution, H^{+} , to form $\text{Mn}^{2+}(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$

10. Write the net equation for (a)–(d) above.

Answer



11. Calculate the E° for the net reactions.

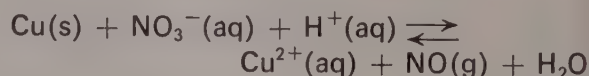
Answer

- (a) 2.09 volts; (b) 0.30 volt; (c) -0.59 volt; (d) 1.35 volts.

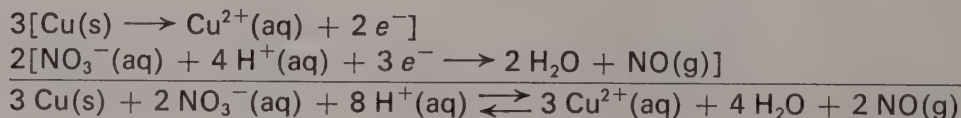
12. Which of the reactions, if any, does not occur spontaneously?

Answer: (c).

13. Write a balanced equation for this oxidation-reduction reaction, using the half-reaction method.



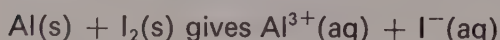
Answer



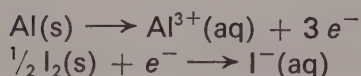
14. Name the oxidizing agent in question 13.

Answer: NO_3^{-} .

15. Write a balanced equation, using the half-reaction method.



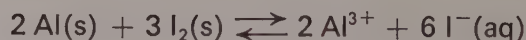
Answer



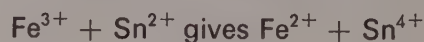
Three iodide ions must be formed for each aluminum atom:



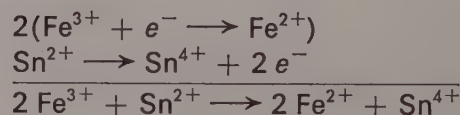
or



16. Write a balanced equation for



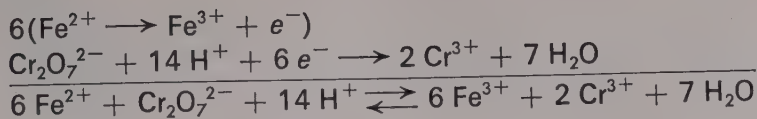
Answer



SUGGESTED QUIZ QUESTIONS

17. Write a balanced equation for: $\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + \text{H}^+$ gives $\text{Fe}^{3+} + \text{Cr}^{3+} + \text{H}_2\text{O}$

Answer

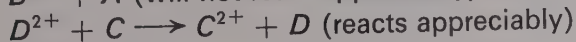
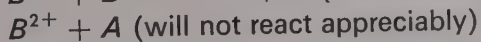
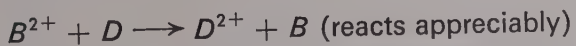


18. Select the compound in which chlorine is assigned the oxidation number +5.

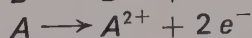
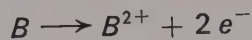
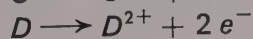
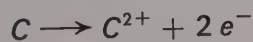
- (a) HClO_4
- (b) HClO_3
- (c) HClO_2
- (d) HClO
- (e) HCl

Answer: (b).

19. Four hypothetical elements *A*, *B*, *C*, and *D* form the aqueous ions A^{2+} , B^{2+} , C^{2+} , and D^{2+} . The following statements indicate some reactions which can, or cannot, occur. Use these data to arrange the metal-ion couples into a short oxidation-reduction potential series, putting at the top the oxidation half-reaction which has the greatest tendency to release electrons.



Answer



20. Which of the following will oxidize I^- to I_2 but not Br^- to Br_2 ?

- (a) Fe^{3+} to Fe^{2+}
- (b) Fe^{2+} to Fe
- (c) Sn^{2+} to Sn
- (d) MnO_4^- to Mn^{2+}
- (e) Na^+ to Na

Answer: (a).

21. Using "T" and "F" indicate whether the following statements are true or false.

- (a) Iron metal can reduce Fe^{3+} to Fe^{2+} .
- (b) Copper metal can dissolve in nitric acid, liberating H_2 gas.
- (c) Oxygen in moist air can oxidize Fe^{2+} to Fe^{3+} .
- (d) Nickel can reduce Sn^{2+} to Sn , but cannot reduce Co^{2+} to Co .

Answer

- (a) T.
- (b) F.
- (c) T.
- (d) T.

Molecular Structure



Intent and Approach

This chapter provides answers to the student who may have asked you, "How is the geometry of a substance determined?" In addition, the concept of isomerism, introduced in this chapter, will be useful in Chapter 18.

A central idea is the importance of structure as contrasted with composition alone. Up to this point in the course, the student has not encountered many instances in which a given formula can represent more than one compound. Isomerism is not an essential idea in a beginning

study of inorganic chemistry.

The isomerism of ethanol and methyl ether forms a continuous thread through this chapter. In Sections 16-1 and 16-2 the student follows the reasoning that originally led to the recognition of their differences. That is, by comparing their chemical behavior with known compounds, two formulas are derived. In the latter sections, 16-3 to 16-6, the use of spectroscopic methods is illustrated with the same pair of compounds.

Outline

Section 16-1 considers composition and structure by means of various kinds of formulas (empirical, molecular, structural). In Section 16-2 ethanol is used as an example.

The interaction of energy with matter is taken up in Section 16-3.

The next three sections deal with particular types of energy interactions: diffraction, mainly of X rays (16-4), infrared spectroscopy (16-5), and nuclear magnetic resonance, NMR, (16-6).

A review (16-7) follows.

New Concepts

1. The importance of structure in determining chemical behavior.
2. The determination of molecular structure from

methods measuring energy interaction with the molecule.

DEVELOPMENT

SCHEDULE AND RELATED MATERIAL

Suggested Time: 5 days

Text Section	Topic and Other Work	Exercises	Problems		
			Easy	Medium	Hard
16-1	Different Kinds of Formulas	1	1	4	2, 3
16-2	Determination of the Structure of Ethanol	2-5	5	6-8	9, 10
16-3	Energy and Molecular Structure			11	
16-4	Diffraction Methods <i>Film:</i> Crystals and Their Structures				
16-5	Spectroscopic Methods <i>Film:</i> Molecular Spectroscopy		12, 13	14	
16-6	Nuclear Magnetic Resonance		15-17	18-20	21
16-7	Review				

Note: Experiment 37 can be done any time during Chapter 16.

Development

CHEMICAL METHODS OF STRUCTURE DETERMINATION

16-1 Different Kinds of Formulas

The Empirical Formula. Before starting to describe the various formulas and how they are found, it is worthwhile reminding the student that this is not an idle exercise. Every compound must be carried through this process before it can be called "known."

Earlier in the course, we usually encountered empirical formulas in situations where *only* that kind of formula can be found. There is no molecular formula for solid SiO_2 or NaCl . Emphasize *isomers*, which he has not had to use much before, and make it clear that they arise because there are many ways to connect the same atoms. Be sure to use the mole method, not weight-percent, in calculating empirical formulas.

The Molecular Formula. This reduces to a molar mass determination, then enough empirical formula units are taken to give the molar mass.

The Structural Formula. The Textbook adequately describes (in Section 16-2) the use of reaction differences to decide between possible

isomers. There are other methods, however, one of which consists in synthesizing the compound in a way that furnishes final proof of the structure.

16-2 The Determination of the Structure of Ethanol

The methods described in the preceding section are applied to ethanol. The main new point for the student is in the last question, "How are the atoms arranged?" Textbook Figure 16-2 shows one way to arrive at possible structures using only the number of each kind of atom and their normal bonding capacity. The structures of a huge number of compounds were found in this way. Note that the concept of functional groups makes such a search much easier. The student will study functional groups in Chapter 18.

PHYSICAL METHODS TO DETERMINE MOLECULAR STRUCTURE

16-3 Energy and Molecular Structure

Build this section on Chapter 8 in which the interaction of light (visible and ultraviolet) with

atoms was studied. Recall that energy comes in quanta of many sizes. Some are just right for one type of interaction with matter; others are suitable for another type of interaction. We have the same situation with our money. A dime is just right to get a soft drink from a machine, a dollar is not usable.

16-4 Diffraction Methods

Film, CRYSTALS AND THEIR STRUCTURES,

fits here. See p. 326 for summary.

The phenomenon of X-ray diffraction is treated empirically. The student is told that X rays reflect from a crystal to give patterns that reveal the spacing and arrangement of atoms. Constructive and destructive interference are not mentioned. Figure 16-8 (Textbook) shows the type of line-pattern obtained from a finely divided sample (a "powder" pattern).

X-ray diffraction methods for determining the spacing of atoms in crystals arose from Max von Laue's prediction, made in 1912, that crystals would give a diffraction pattern if the wavelength of the light used was as small as the distance between the atoms in the crystal. Two English scientists, W. H. Bragg and his son

W. L. Bragg, found that the scattering of X rays can be explained as a reflection of the rays by successive layers of atoms in the crystal. At a definite angle θ , between the beam of wavelength λ and the atomic layers in the crystal, the reflections of the different layers reinforce one another. The equation is

$$n\lambda = 2d \sin \theta$$

where n is an integer and d is the distance between the reflecting layers.

The experimental data are compared with calculated diffraction patterns based upon reasonable models. Different packing arrangements imply different interlayer spacings (differing values of d), and hence different diffraction patterns. The packing arrangement and the assumed atomic radius are varied until a model is found that reproduces the observed pattern. For simple packing arrangements (as in metals and simple ionic solids), it is not too difficult to find the appropriate parameters. For molecular crystals, however, analysis is much more difficult.

In current research, electronic computers play a big and increasing role. In some installations they control the X-ray apparatus during data taking and then process the result. Finally, the computer feeds calculations to a plotting machine which draws two stereoscopic views of the structure. Figure 16-1 contains such a pair of

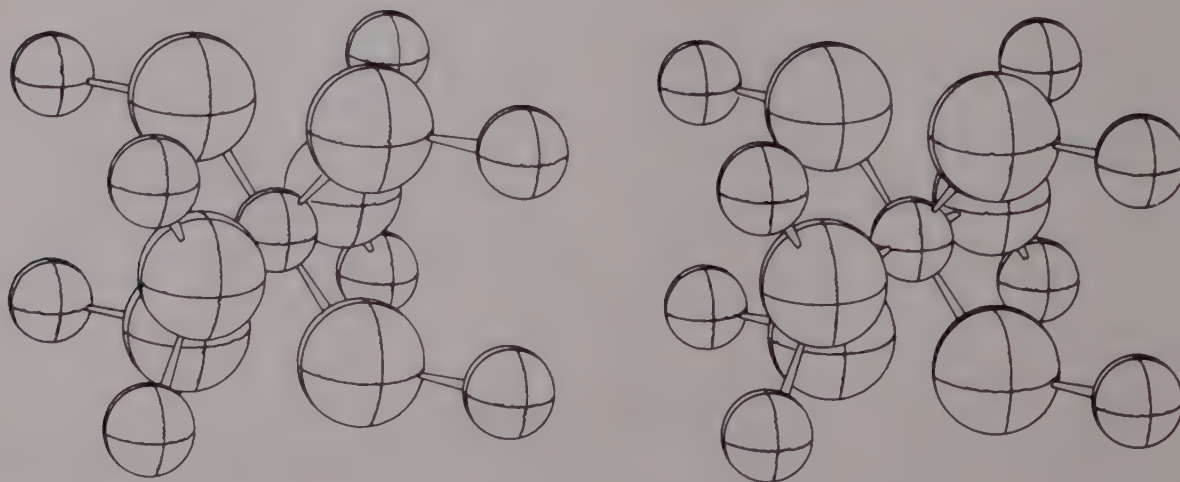


FIGURE 16-1

Computer derived and plotted stereoscopic views of part of a TiO_2 crystal.

drawings for part of a TiO_2 crystal. Use a stereoptican viewing device or get the three-dimensional view to appear by focusing your eyes some distance behind the page.

X-ray methods are applicable to solids over a wide temperature range. The methods are not applicable to the gas phase, and in X-ray studies of liquids the scattering patterns are difficult to interpret because of the disordered packing of the molecules. In none of the phases are hydrogen atoms located precisely.

The two other methods mentioned in this section are used less than X-ray diffraction. Electron diffraction is applicable only to gases because the degree of scattering from condensed phases is too large.

Neutron diffraction has come into use since the advent of high flux neutron beams from nuclear piles. This technique is important because it locates hydrogen atoms quite precisely. Since there are not many piles, neutron diffraction is used less frequently than X-ray diffraction.

16-5 Spectroscopic Methods

Although Textbook Table 16-1 lists spectroscopic ways to study vibration and rotation, more emphasis is placed on molecular vibration than on rotation. The reason is that the existence of characteristic, or "resonant," vibrational frequencies in a vibrating system is common (tuning forks, cymbals, vibrating strings, etc.). This emphasis is appropriate, since the vibrational spectroscopy is more widely applicable (solids, liquids, and gases) and is far more commonly used. Each molecular species has an absorption spectrum that can be likened to a fingerprint. Hence the spectrum has obvious value for anal-

ysis, both qualitative and quantitative.

Film, MOLECULAR SPECTROSCOPY,

fits here. See p. 326 for summary.

The results for ethanol and methyl ether are used to illustrate infrared spectroscopy. We have called the student's attention to only two lines although there are clearly more. The pupil who asks about the other peaks can be told they result from other vibrations. In particular, C—C and C—O stretching plus C—H and O—H bending vibrations.

16-6 Nuclear Magnetic Resonance, NMR

Nuclear magnetic resonance has the same potentialities discussed for infrared spectroscopy. The method depends upon nuclear magnetic properties that cause some nuclei to absorb microwave frequencies when they are subjected to a high magnetic field. The actual frequencies absorbed reveal the type of nucleus and its chemical environment.

Again ethanol and methyl ether are used as examples. Information about the types of protons and their number is not so easy to get by other techniques. The NMR method has a disadvantage not shared by infrared spectroscopy. It can detect only certain nuclei. Some common nuclei that give the effect are ^1H , ^2H , ^{13}C , ^{14}N , ^{17}O , ^{19}F , ^{35}Cl , ^{37}Cl . Fortunately ^{12}C , ^{16}O , ^{18}O , and ^{32}S do not possess nuclear magnetic moments. Therefore no resonance lines come from them. Otherwise NMR spectra would be much more complex.

16-7 Review

Supplementary Material

Articles

G. C. Pimentel, "Infrared spectroscopy, a chemist's tool," *J. Chem. Education*, **37**, 651–657 (1960). Useful for teacher; suitable for advanced student.

Books

G. M. Barrow, *PHYSICAL CHEMISTRY*, McGraw-Hill, New York (1966). Chapter 10 provides an *excellent background in depth for the teacher*, but is too advanced

for the high school student. The chapter covers rotational, vibrational, and electronic spectroscopy in quantitative detail.

G. M. Barrow, *THE STRUCTURE OF MOLECULES* (paperback), W. A. Benjamin, Inc., New York (1963). An essentially nonmathematical book for beginners. Chapters 1 and 3 are especially appropriate. The others go into rotation and emission spectroscopy.

W. S. Brey, Jr., *PHYSICAL METHODS FOR DETERMINING MOLECULAR GEOMETRY* (paperback), Reinhold Publishing Corp., New York (1965). Chapters 1-3, 7, and 8 are suitable for this chapter. Chapter 4 covers dipole moments and is thus useful in our Chapter 17.

J. R. Dyer, *APPLICATIONS OF ABSORPTION SPECTROSCOPY OF ORGANIC COMPOUNDS*, Prentice-Hall, Inc., Englewood Cliffs, N. J. (1965). Chapters 3 and 4 are on infrared and NMR spectroscopy. Especially good for teachers; could be read by better students.

Films

For ordering information see the *List of Film Sources* at the back of the Teacher's Guide.

CRYSTALS AND THEIR STRUCTURES

A CHEM Study film

Running Time: 22 minutes

Professor J. Arthur Campbell, of Harvey Mudd College, collaborated in producing this film and appears in it. He demonstrates some common crystalline properties (plane faces, sharp melting points, cleavage) and introduces diffraction of X rays. Such properties lead to the belief that crystals are composed of regular repeating arrangements of atoms. How we discover these arrangements is illustrated by experiments done in a ripple tank, giving direct observation of the type of measurement by which actual structures are determined.

Note that since Bragg's Law is used in the calculations, questions may be raised about the sine of an angle θ . Answer this simply by explaining that, in a right triangle, it is the ratio of the side opposite the angle θ over the hypotenuse.

MOLECULAR SPECTROSCOPY

A CHEM Study film

Running Time: 23 minutes

This film was produced with the collaboration of Professor Bryce Crawford, Jr., of the University of Minnesota. Professor Crawford, who appears in the film, is one of the foremost molecular spectroscopists in the world. The film correlates well with the textbook discussion of the properties of light and of infrared spectroscopy. It adds more depth in microwave spectroscopy. Topics taken up include:

1. The dispersion of white light into a spectrum: color and frequency.
2. The existence of energy in wave form beyond both ends of the visible spectrum.
3. The details of constructing and operating a spectrometer.
4. Resonant vibration frequencies demonstrated with a ball-and-spring molecular model of CO_2 .
5. The isotope effect observed for HCl and DCl.
6. The difference between the infrared spectra of CHCl_3 and CCl_4 and its use in quantitative analysis of mixtures.
7. The quantization of rotational energy levels.

This film will be a valuable aid in the difficult task of introducing spectroscopy without the background of a prior physics course.

Background Discussion

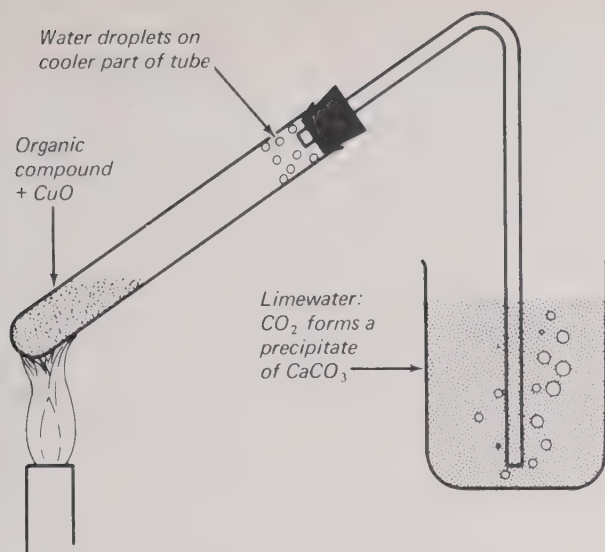
DETERMINING THE COMPOSITION

Some students may be interested in how the composition is determined. These qualitative tests can be described or done by some students.

The first step is to determine the elements contained in the compound. A test for carbon is conclusive and can be quickly (and qualitatively) done by the CuO method (Figure 16-2). When an organic compound is mixed with copper oxide (CuO) and strongly heated, CO_2 and water are formed and can be detected (identified) by con-

ventional tests.

After establishing that the substance does contain carbon (and hydrogen), it becomes interesting to know what other elements it contains. Oxygen, sulfur, nitrogen, and the halogens are most frequently found. For many inorganic compounds qualitative analysis consists of tests for the anions (e.g., Cl^- , SO_4^{2-} , NO_3^- , H_2PO_4^- , etc.) and cations (e.g., Na^+ , Mg^{2+} , Fe^{2+} , Al^{3+} , Cr^{3+} , etc.) of which they are composed. In most organic compounds that contain a halogen, nitro-

**FIGURE 16-2**

The CuO test for carbon and hydrogen.

gen, and sulfur, these elements are present in covalent combination and do not dissociate as separate ions when the compound is dissolved in a solvent. Thus a test for Br^- that will be successful for sodium bromide will not give a positive result for a compound such as bromobenzene, $\text{C}_6\text{H}_5\text{Br}$, which is a liquid compound of negligible solubility in water.

Since at this stage in the investigation we are not concerned with *how* a bromine, nitrogen, or sulfur atom is bonded to the other atoms of our unknown compound, but only with the presence or absence of these in the compound, the experimental method used consists in subjecting the compound to drastic treatment with a reagent that will free the elements in question from their organic combination and permit us to apply the usual tests to detect their presence.

The usual procedure is to heat the compound strongly (up to a red heat) with metallic sodium. Extensive decomposition occurs, and halogens, nitrogen, and sulfur are converted into halide ions, sulfide ions, and (with the carbon that is present) cyanide ions. The analysis is completed by testing a water solution for these ions. These tests can be found in any text on experimental organic chemistry. Figure 16-3 shows the procedure.

CHEMICAL EVIDENCE FOR THE EXISTENCE OF ATOMS

The logic by which chemical evidence leads to the atomic hypothesis is direct.

1. *There are compounds and elements.* Operationally, an element is a substance that *cannot* be decomposed into two or more distinct substances, and a compound is a substance that *can* be decomposed into two or more distinct substances.
2. Compounds are found to have definite composition (in terms of the relative masses of the elements contained). That there are some exceptions to this statement (for example, $\text{Cu}_{1.8-2.0}\text{S}$) does not deny its general validity. Definite composition does not of itself prove the existence of atoms—it is consistent with their existence. Lack of definite composition does not disprove the existence of atoms—the lack is explained by assuming that some of the positions in the crystal structure are vacant.
3. When two elements are combined in two different compounds, the masses of one element reacting with a fixed amount of the other are related by ratios of simple whole numbers (the law of *simple multiple proportions*).
4. Gases react in simple proportions by volume, and the volume of any gaseous product bears a whole number ratio to that of any gaseous reactant (the law of *combining volumes*).

The first evidence for the existence of elements and compounds is consistent with, but does not imply, the atomic hypothesis. This is shown by the differentiation between elements and compounds that had been made centuries before Dalton proposed the atomic hypothesis.

The second evidence raises real questions about the structure of matter. Why do elements react only in certain ratios? This fact causes one to consider models of the structure of matter—models that would “explain” the definite composition of compounds. Once again, however, the evidence is consistent with (in an intuitively satisfying way) the atomic theory, but does not suggest it by itself.

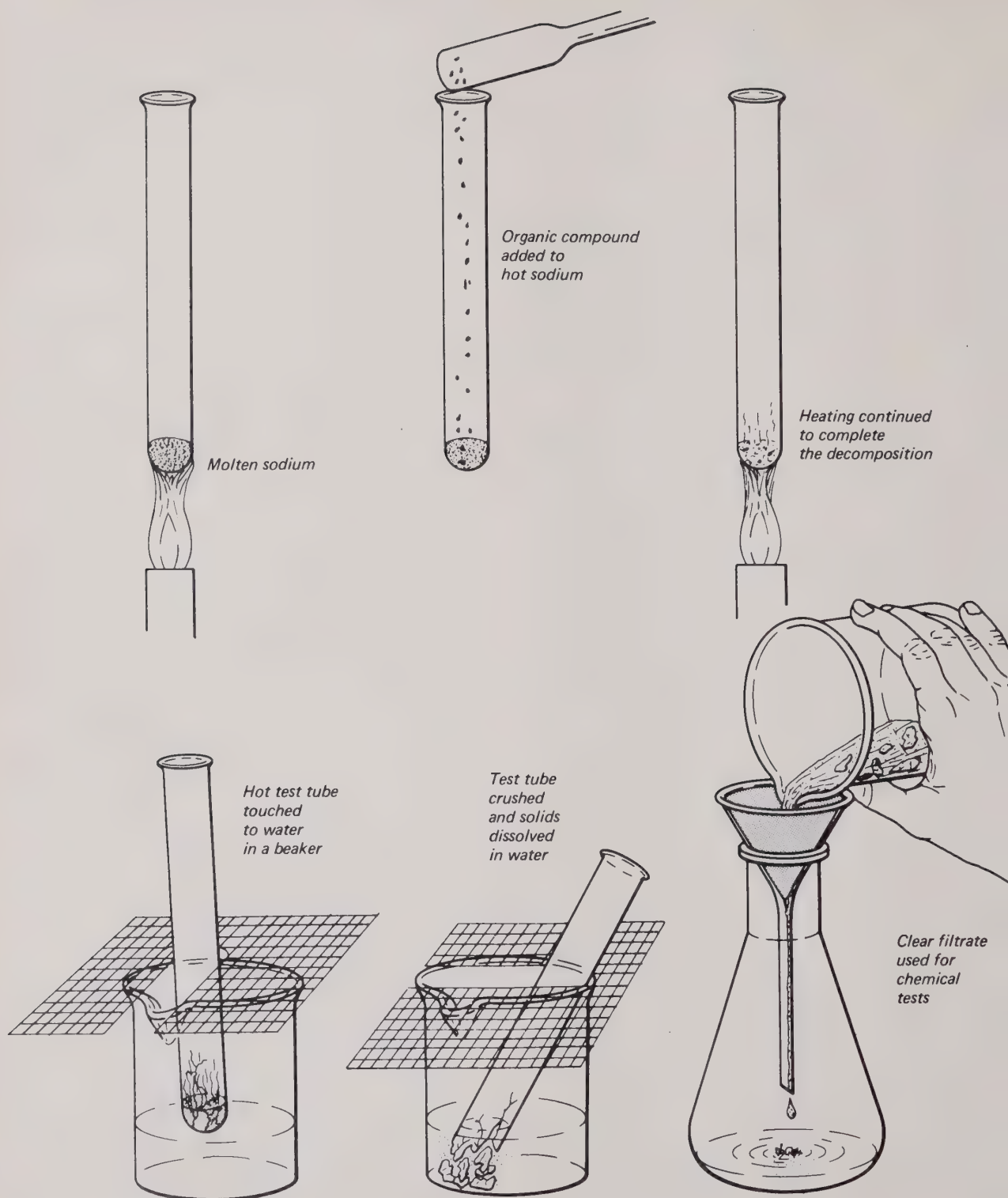


FIGURE 16-3

The sodium fusion test for halogens, S, and N atoms in an organic compound.

BACKGROUND DISCUSSION

The third evidence *does* suggest the atomic hypothesis. Simple integer relationships suggest "units" or "portions." A given amount of oxygen can react with one "portion" of hydrogen, or two "portions," but not 1.8732 "portions." These simple integer relationships interweave all of chemistry, relating the compositions of compounds. Thus the composition of NH_3 is simply related to the compositions of NO and H_2O_2 .

0.0625 g hydrogen reacts with 1.000 g oxygen
(in H_2O_2)

0.8750 g nitrogen reacts with 1.000 g oxygen
(in NO)

3(0.0625) g hydrogen reacts with 0.8750 g nitrogen
(in NH_3)

Such evidence naturally leads to a model involving "portions," "particles," or, finally, atoms.

The fourth evidence again involves simple integer relationships, but in quite another way—the volumes are related simply. Two volumes of hydrogen react with one volume of oxygen and produce two volumes of water vapor (all at the same temperature and pressure). Once again these integer relationships lead to models made up, somehow, of "units" or "portions," and point the way to the atomic hypothesis.

Once the atomic model is proposed, we need only verify that it is consistent with the known facts. The student himself knows that such a theory is consistent with many experiments he has done and is, no doubt, ready to believe that the theory does pass this test.

This is the substance of the logic by which chemical evidence supports the atomic theory. Most students who take high school chemistry will understand this reasoning. The atomic theory occupies such a central position in chemistry that this logic should be presented in the sharpest possible focus.

EVIDENCE FOR THE EXISTENCE OF ATOMS FROM MOTIONS OF ATOMS AND MOLECULES

Other evidence for the existence of atoms and molecules is contained in a number of observa-

tions best explained in terms of motion. According to Newton's laws of motion, applicable to all visible bodies, momentum (mass $\times$ velocity) is conserved (when net force is zero).

$$\Delta(mv) = 0$$

The force, f , required to accelerate bodies is equal to the product of the mass, m , and the acceleration, a ;

$$f = ma$$

The kinetic energy of a moving body is

$$\text{K.E.} = \frac{1}{2}mv^2$$

If quantitative explanations are made possible by assuming that these same relations apply to the postulated invisible particles, atoms and molecules, we can be more certain of their existence. This is true with regard to a variety of phenomena.

Gas Behavior

In 1738, Daniel Bernoulli, a Swiss mathematical physicist, explained gas pressure in terms of the rapid motion of small particles of gas. In 1748, M. Lomonosov, a Russian scientist, suggested a kinetic theory to explain both pressure and temperature effects in gases. These brilliant, early proposals of the atomic hypothesis seem to have had slight impact in promoting the atomic view of the structure of matter. The detailed kinetic theory of gases was not developed until about one hundred years later (1860–1890), after the atomic theory had been deduced from chemical evidence.

The kinetic theory of gases, devised for "ideal" gases (consisting of particles with mass but negligible volume and negligible attraction for one another), predicts remarkably well the behavior of real gases. It is in accord with PVT behavior, Avogadro's Hypothesis, effusion rates, diffusion phenomena, and viscosities. Furthermore, the rates of effusion and diffusion of different gases are those predicted by the kinetic theory for particles with masses equal to the chemist's molecular masses.

Diffusion in Condensed Phases

The diffusion of substances in liquids, and its dependence on temperature, lends further support to the idea that particles (atoms, molecules, and ions) in liquids are in motion and that their motion increases with increasing temperature. Kinetic effects in solids are harder to observe, but it is necessary to postulate the motion of particles in solids to explain their melting, evaporation, and solution to form liquids and gases, in which kinetic effects are visible.

Gases at Low Pressures

Many of the experiments described in the chapter take place in vacuum tubes in which some new effects appear. The particle theory of gases helps us to interpret them.

A 245 ml flask holds 0.01 mole (25°C, 1 atmosphere) and about 6×10^{21} molecules of gas. If a good vacuum pump is used to lower the pressure to 10^{-8} atmosphere, 10^{-10} mole, or 6×10^{13} molecules, will remain. Although this is a large number of molecules, collisions between them will almost disappear. That is, the average distance traveled by a particle between collisions, called the *mean free path*, will be very large. If there are n particles of diameter d in each milliliter, their mean free path in centimeters will be

$$\text{mean free path} = \frac{1}{\sqrt{2} \pi n d^2}$$

In a gas at atmospheric pressure and 25°C the number of molecules per milliliter is approximately 2.5×10^{19} . If the molecular diameter is 3×10^{-8} cm the mean free path is 1×10^{-5} cm. The mean free path under these conditions is 330 times the molecular diameter and approximately thirty times the average distance between molecules. If the pressure and number of molecules are reduced to one-millionth (10^{-6}) of the initial values, the mean free path increases to 10 cm. At 10^{-8} atmosphere the mean free path becomes 1000 cm. In an ordinary-sized vessel, collisions between molecules become rare at this pressure—most collisions are with the walls of the vessel.

In a gas-filled tube like that in Figure 8-5 (Textbook p. 127), any electrons sent into the gas phase will collide with gas molecules and be scattered. When the amount of gas is reduced, the mean free path of the electrons increases, with the result that, between collisions, they can be accelerated to high speeds by the electric field. Then they collide with more energy and produce gaseous ions from the gas molecules. The color comes from the excited ions. At low enough pressures most of the electrons can travel to the end of the tube without collisions. As a result few ions are produced, and the glow is lost again.

INFRARED SPECTROSCOPY

The absorption of energy in the infrared spectral region is connected with vibrational motions within the molecule. The frequencies are fixed by the molecular geometry and by the strengths of the chemical bonds. Since the spectra are readily obtained for the solid, liquid, and gas phases, the infrared technique is probably the most important and most used by the chemist. Infrared spectra are recorded as a routine part of the laboratory work in undergraduate chemistry courses at the university level. In organic chemistry, the infrared spectrum has assumed a role as important as the melting temperature for identifying compounds.

Interpretations of infrared spectra are based upon an analysis of how the molecular energy depends upon the internuclear distance. Such a potential energy function can be used because the motions of the nuclei are so slow compared to the motions of the electrons. As the nuclei vibrate about their equilibrium positions, the electron distribution readjusts continuously. Thus the molecular energy changes to the new energy required by the less-than-optimum internuclear distance. This separation of electron motion and nuclear motion is called the Born-Oppenheimer approximation.

Since a plot of molecular energy as a function of internuclear distance relates energy to position, it is appropriate to call this a potential energy

plot, or in common usage, a "potential function." The solid line in Figure 16-4 shows a typical

plot of molecular energy versus internuclear distance for a diatomic molecule.

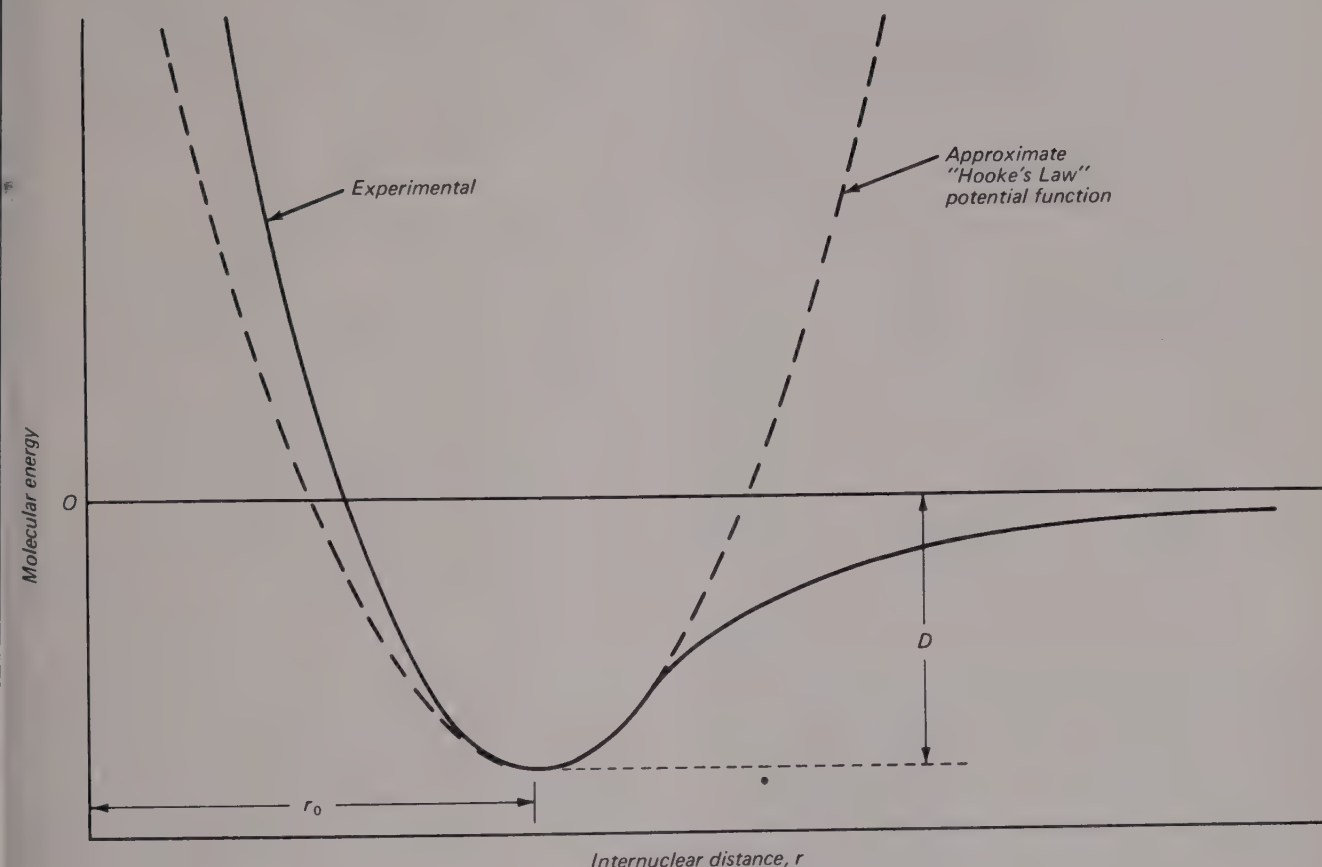


FIGURE 16-4

Molecular energy versus internuclear distance for a diatomic molecule.

Figure 16-4 shows that the molecular energy is lowest when the internuclear distance is r_0 . This fixes the equilibrium bond length. If there is any change of bond length, the energy rises, establishing a restoring force. Thus the molecular energy acts like a spring insofar as the slow movements of the nuclei are concerned. The molecular energy fixes the potential function for the vibrational movement of the atoms.

To treat the problem quantitatively, the potential function is approximated by the parabola of closest fit, as shown by the broken line in Figure 16-4. This curve has the simple mathematical form

$$V(r) = \frac{1}{2}k(r - r_0)^2 = \frac{1}{2}kx^2$$

where $x = r - r_0$ = displacement from equilibrium distance. The restoring force implied by this potential function is

$$F = kx$$

which is just Hooke's Law of force, commonly applied in the vibrations of objects connected by springs. The last equation is called the "harmonic approximation." The restoring-force constant, k , is determined mathematically by the curvature of the potential function, $V(r)$, at the equilibrium distance. In practice k comes from the frequency

of absorption and the masses of the vibrating atoms.

The value of learning k is that it is a measure of the strength of the chemical bond. In fact there are generally linear relationships for a given pair of atoms among the following: the energy needed to break a bond (D in Figure 16-4), the

length of bond (r_0), the force constant (k), and the bond multiplicity. Table 16-1 shows some data applicable to carbon-carbon bonds and to nitrogen-nitrogen bonds. The stronger bonds (higher bond multiplicity) clearly have shorter bond lengths and higher force constants.

TABLE 16-1
Correlations Among Bond Order, Bond Length, and Force Constant

Bond Between	As in	Bond Multiplicity	Bond Length (Å)	Force Constant (dynes/cm)
C—C	ethane	single	1.54	5×10^5
C=C	ethylene	double	1.34	10×10^5
C≡C	acetylene	triple	1.21	16×10^5
N—N	N ₂ H ₄	single	1.47	4.5×10^5
N=N	N ₂ F ₂	double	1.25	13×10^5
N≡N	nitrogen	triple	1.10	23×10^5

The vibrational spectra of polyatomic molecules are more complicated, of course, than those of diatomic molecules. Fortunately, certain functional groups have characteristic vibrational frequencies. Hence the infrared spectrum provides a valuable diagnostic tool for various bond arrangements. Table 16-2 shows some characteristic absorption frequencies for various groupings. It is evident that the vibration frequency is indicative of the chemical bonding. By recording an infrared spectrum and making a careful analysis of the spectrum, a chemist can learn much about the molecular structure of an unknown compound.

NUCLEAR MAGNETIC RESONANCE

This is a modern technique. It is based rather directly on work for which Felix Bloch and Edward Purcell shared the 1952 Nobel Prize in Physics. Nevertheless, it has quickly become a very important method for determining structure. The method depends on detecting absorption of energy which is interpreted as a change in the orientation of magnetic nuclei under the influence

of both a magnetic field and a proper kind of radio energy.

Nuclei have mechanical spin, described by a spin number which can have integral or half-integral values. As the nuclei are also charged, a magnetic field results from the spinning charge. The spin number, usually called I , can be 0, $\frac{1}{2}$, 1, $\frac{3}{2}$, 2, $\frac{5}{2}$, ... and so on. The value of I is related to mass number and atomic number in one of three simple ways.

(1) If mass and atomic number are *even*, I is zero. Thus many of the commonly-occurring nuclei (¹⁶O, ¹²C) have $I = 0$ and do not possess a magnetic moment. In a sense this is a convenient fact. If all atoms in a sample were active the NMR spectrum would be very much more complex.

(2) If mass number is even but atomic number is odd (¹⁴N), an integral value of I is found.

(3) When mass number is odd, I is half-integral, regardless of atomic number. The proton (¹H) fits this group and has $I = \frac{1}{2}$. This is the only element considered in the Textbook discussion of NMR. There are two reasons. First,

TABLE 16-2

Characteristic Absorption Frequencies for Stretching Some Common Chemical Bonds

Functional Group	Frequency Range in Which Absorption Occurs (cycles/sec)
O—H	11.0 to 10.8×10^{13}
N—H	10.5 to 9.9×10^{13}
C—H (paraffins)	8.9 to 8.5×10^{13}
C $\equiv$ C—	6.8 to 6.3×10^{13}
C=O	5.5 to 5.0×10^{13}
C=C	5.0 to 4.9×10^{13}
C—F	4.2 to 3.0×10^{13}
C—Cl	2.4 to 1.8×10^{13}
C—Br	1.8 to 1.5×10^{13}

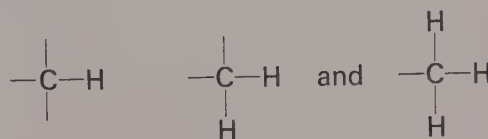
most NMR work is done with proton spectra. Second, a spin number of $1/2$ gives the easiest case to explain as there are just two possible arrangements of the spinning nucleus. Therefore there are just two magnetic energy levels. The number of levels is given by $(2I + 1)$.

Transition of the proton between the two levels requires $E = h\nu = 2\mu H$ (μ is the magnetic moment and H the magnetic field). One common instrument uses a 14,000 gauss field which means this proton transition requires a frequency of about 60 megacycles/sec to give the proper energy. The latest spectrometers use even higher fields and frequencies to give greater sensitivity.

In the Textbook we have discussed the resonance effect as though a bar magnet were flopping from perfect alignment parallel to the field into a perfectly antiparallel, or opposed, position. A more thorough treatment would reveal that the nucleus is rarely so aligned. Rather it is at an angle to the field. As a result it is not fixed in position but is *precessing*. That is the spinning axis traces a circle at right angles to the field. The precession or Larmor frequency is what is loosely called the frequency of flopping.

At normal laboratory temperatures there is very little difference in the number of protons in the high and low energy states. Perhaps 0.001% more occupy the low energy state. This means for every million protons, 500,010 are of low energy and 499,990 of high. This very small fractional difference is sufficient, with current skill in electronics and magnet construction, to allow almost routine operation of the spectrometer.

To a chemist the *chemical shift* is the most interesting aspect of NMR measurements. The term describes the fact that all protons do not resonate at the same radio frequency. The occurrence of shifted positions has been correlated with the *shielding* caused by the electrons near the proton. That is, a proton attached to an oxygen (or nitrogen) atom is considered by chemists to have electrons drawn toward the electron attracting atom. Such a proton is more nearly "bare" than one bonded to a carbon (or silicon) atom, which has less electron attracting ability. The resonance method is so sensitive that the small differences between



groups can usually be distinguished with ease. Special bonding arrangements (as in acetylene, benzene, and hydrogen bonded molecules) cause additional shielding or deshielding. The peaks for protons near such environments are shifted by additional amounts. This chemical shift is alluded to in the Textbook as the reason for the

three peaks in the ethanol spectrum. Such shifts are measured from some reference, often $\text{Si}(\text{CH}_3)_4$, tetramethylsilane or TMS.

Another effect, not discussed in the Textbook, is very useful in diagnostic work. This is the

spin-spin interaction between protons (or other magnetic nuclei) in the same molecule. The effect is illustrated in Figure 16-5 which reproduces a high resolution spectrum of acidified ethanol.

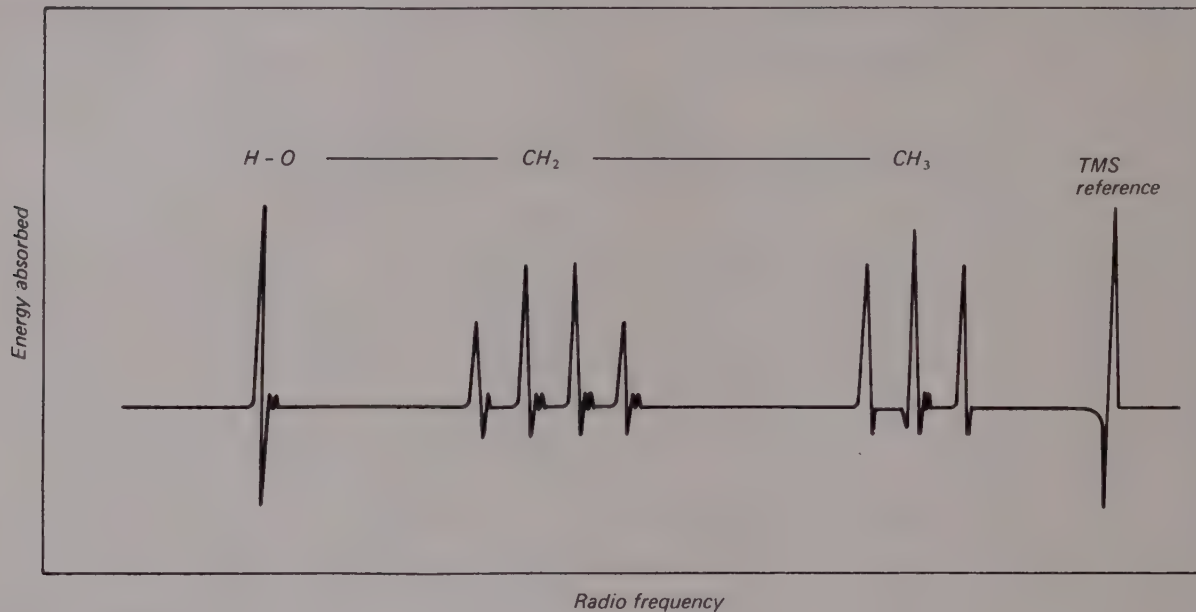


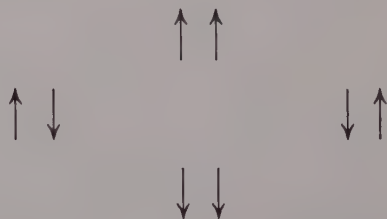
FIGURE 16-5

High resolution NMR spectrum of ethanol showing spin-spin splitting.

We see that the three peaks presented to the student in Textbook Figure 16-12, p. 326 (compare) are now split into multiples in two of the peak regions. This splitting results from the effect of nearby nuclear magnets.

The OH proton is not affected, largely because it is separated from other protons by an atom which attracts electrons avidly. On the other

hand the methylene and methyl peaks are split. The methyl protons produce three peaks—but *not* because there are three of them. Rather three lines occur because there are three unique ways the two adjacent methylene protons may be arranged relative to the magnetic field. These possibilities are indicated by these diagrams

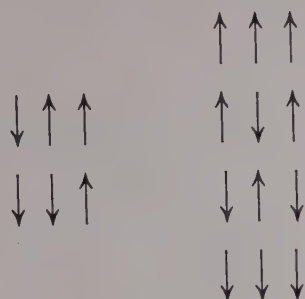


(these two are equivalent)

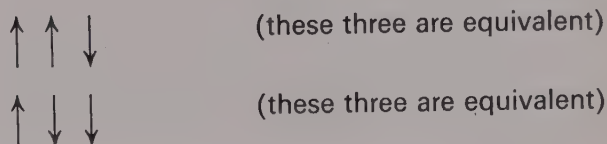
Note in Figure 16-5 that the three methyl peaks are of two sizes. The center one encloses twice the area of one of the smaller ones. Such a result is expected since one arrangement occurs

twice as frequently. We see all three lines because among the tremendous number of molecules in the sample there are some possessing each of the possible arrangements.

In a similar way, the two methylene protons produce four peaks when under the influence of the splitting fields of the methyl proton arrange-



ments. There are four uniquely different ways to align the three magnetic moments of the methyl protons. They are



Again the number and size of the peaks agrees with the possible arrangements.

A careful study of the splitting pattern is a

great help when an unknown is under test. Often the number of structures to be considered can be severely limited by this criterion.

Answers to Exercises and Problems

Exercise 16-1

Write the molecular formula for the carbon-hydrogen compound having the empirical formula CH_2 and a molar mass of 28 grams.

Answer

CH_2 has a molar mass of 14 g. It requires two such units to give molar mass 28 g. The molecular formula is $(\text{CH}_2)_2$ or C_2H_4 .

Exercise 16-2

Automobile antifreeze often contains a compound called ethylene glycol. Analysis of pure ethylene glycol shows that it contains only carbon, hydrogen, and oxygen. A sample of ethylene glycol was burned and the following results were obtained.

mass of sample burned = 15.5 mg
mass of CO_2 formed = 22.0 mg
mass of H_2O formed = 13.5 mg

What is the empirical formula of ethylene glycol?

Answer

$$\frac{0.0220 \text{ g}}{44 \text{ g/mole}} = 0.0005 \text{ mole } \text{CO}_2$$

which contains 0.0005 mole C or 6 mg

$$\frac{0.0135 \text{ g}}{18 \text{ g/mole}} = 0.00075 \text{ mole } \text{H}_2\text{O}$$

which contains 0.0015 mole H or 1.5 mg

Oxygen in the sample equals $15.5 - 6 - 1.5$
or 8.0 mg

$$\frac{0.0080 \text{ g}}{16 \text{ g/mole of oxygen atoms}} = 0.0005 \text{ mole O}$$

C	0.0005 mole	or	1 relative amount
H	0.0015		3
O	0.0005		1

The empirical formula is CH_3O .

Exercise 16-3

Ethylene glycol, the example treated in Exercise 16-2, has an empirical formula of CH_3O . A sample weighing 0.49 gram is vaporized completely at 200°C and at one atmosphere pressure. The volume measured under these conditions is 291 ml. The same volume of oxygen gas at the same conditions weighs 0.240 gram. Is the molecular formula for ethylene glycol CH_3O or $\text{C}_2\text{H}_6\text{O}_2$ or $\text{C}_3\text{H}_9\text{O}_3$ or some higher multiple of CH_3O ?

Answer

According to Avogadro's Hypothesis, the number of molecules (or moles) is equal in equal volumes of gases at the same conditions.

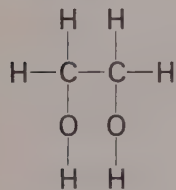
$$\frac{0.49 \text{ g glycol}}{m \text{ g/mole glycol}} = \frac{0.24 \text{ g O}_2}{32 \text{ g/mole O}_2}$$

$$m = \frac{0.49}{0.24} \times 32 = 65 \text{ g/mole glycol}$$

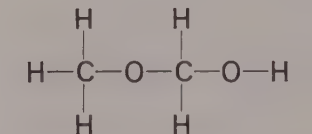
CH₃O has a molar mass of 31 g so two such units would be 62 g. The molecular formula is C₂H₆O₂.

Exercise 16-4

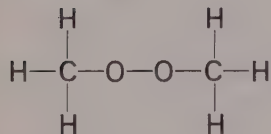
Ethylene glycol has the empirical formula CH₃O and the molecular formula C₂H₆O₂. Using the usual bonding rules draw some of the possible structural formulas for this compound.



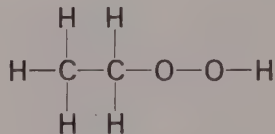
glycol



methyl hydroxymethyl ether



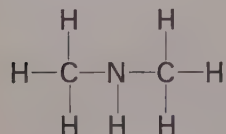
dimethyl peroxide



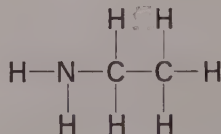
ethyl hydrogen peroxide

Exercise 16-5

Find the possible structures for a compound with molecular formula C₂H₇N. Nitrogen has three unpaired electrons.

Answer

dimethylamine



ethylamine

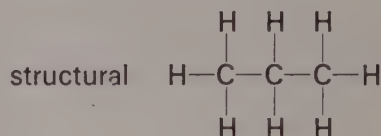
Problem 1

What information is revealed by the empirical formula? The molecular formula? The structural formula? Demonstrate, using propane, C₃H₈.

Answer

The empirical formula gives the *relative* number of atoms of each kind. The molecular formula gives the total number and kind of atoms in one molecule. The structural formula shows the total number of atoms, their kind, and their bond connections:

empirical C₃H₈
molecular C₃H₈

**Problem 2**

A 100 mg sample of a compound containing only C, H, and O was found by analysis to give 149 mg CO₂ and 45.5 mg H₂O when burned completely. Calculate the empirical formula.

Answer

$$149 \text{ mg CO}_2 \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1}{44.0 \text{ g/mole}}$$

$$= 3.40 \times 10^{-3} \text{ mole CO}_2 \text{ containing } 40.8 \text{ mg C}$$

$$45.4 \text{ mg H}_2\text{O} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1}{18.0 \text{ g/mole}}$$

$$= 2.52 \times 10^{-3} \text{ mole H}_2\text{O containing}$$

$$\frac{5.0 \text{ mg H}}{45.8 \text{ mg accounted for}}$$

The oxygen is found by difference

$$100 - 45.8 = 54.2 \text{ mg}$$

$$54.2 \text{ mg O} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1}{16 \text{ g O/mole}}$$

$$= 3.39 \times 10^{-3} \text{ mole O}$$

The moles of each kind of atom are:

	Actual	Relative	
C	3.40×10^{-3}	1	or 2
H	5.04×10^{-3}	1.48	3
O	3.39×10^{-3}	1	2

The empirical formula is $C_2H_3O_2$.

Problem 3

When 0.601 gram of a sample having an empirical formula CH_2O was vaporized at $200^\circ C$, and one atmosphere pressure, the volume occupied was 388 ml. This same volume was occupied by 0.301 gram of ethane under the same conditions. What is the molecular formula of CH_2O ?

One mole of the sample, when reacted with zinc metal, liberated (rather slowly) $\frac{1}{2}$ mole of hydrogen gas. Write the structural formula.

Answer: The molecular formula is $C_2H_4O_2$.

Answer

Equal volumes at identical conditions contain the same number of moles. Hence,

$$\frac{(0.301 \text{ g ethane})}{(30.1 \text{ g/mole})} = 0.0100 \text{ mole ethane}$$

Thus 0.601 gram of unknown equals 0.0100 mole; therefore 60.1 grams are 1.00 mole. The formula must be some multiple of CH_2O . The masses corresponding to various multiples are

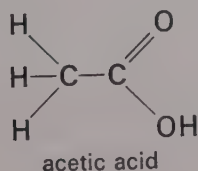
CH_2O	30 g
$C_2H_4O_2$	60 g
$C_3H_6O_3$	90 g

Thus the molecular formula is $C_2H_4O_2$.

The structural formula follows from these facts:

(1) The reaction with Zn to give hydrogen indicates an acid.

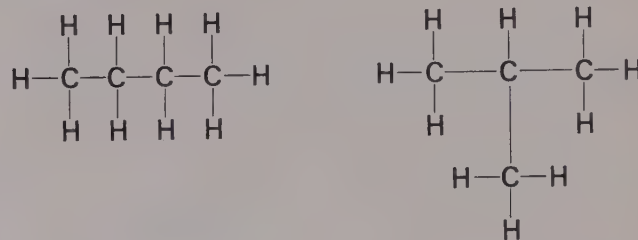
(2) One mole of unknown gives $\frac{1}{2}$ mole of H_2 , indicating that there is only one active hydrogen atom. The formula that best fits these data is



Problem 4

Butane has the molecular formula C_4H_{10} . Draw two different ways of arranging these 14 atoms. Remember carbon usually forms four bonds and hydrogen one.

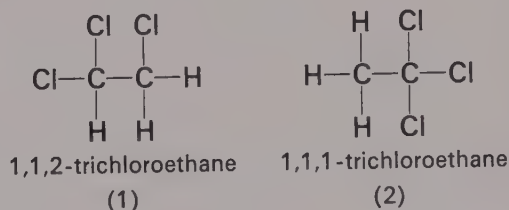
Answer



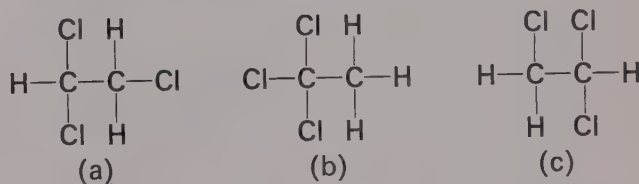
Problem 5

Draw the structural formulas for all the $C_2H_3Cl_3$ compounds.

Answer



There are only two. The following structures, which may appear to be different, are simply different ways of writing the above two:



There are two ways to bring about an apparent change in the structure. One is to rotate the complete molecule; structures (b) and (2) are related in this fashion. The other way is to rotate part of the molecule (along a C—C bond usually) relative to the other part. Structures (a) and (c) are related to (1) by this operation. The structural formulas we draw are really projections of a three-dimensional molecule. Use ball and stick models to illustrate these rotations. Remind the student that kinetic motion will cause the molecules to tumble and spin so that different orientations of a molecule in space do not constitute different isomers. The molecule

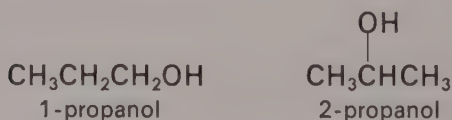
has the same properties no matter how it is turned.

Problem 6

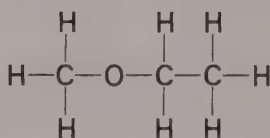
Draw the structure of two isomeric compounds corresponding to the empirical formula C_3H_8O .

Answer

There are two propanols,



and the arrangement

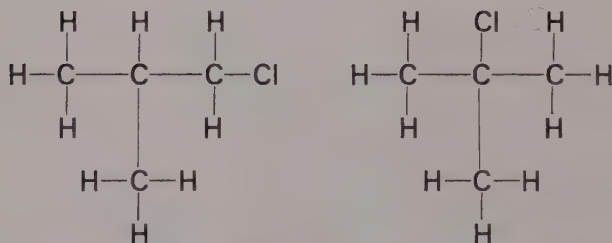
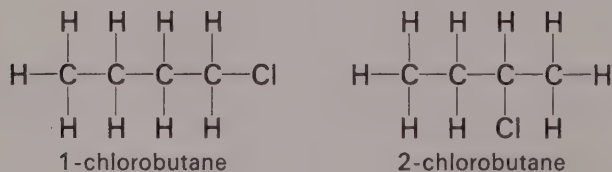


is an isomeric ether.

Problem 7

Draw the structural formulas of the isomers of butyl chloride, C_4H_9Cl .

Answer



1-chloro-2-methyl propane

2-chloro-2-methylpropane

Problem 8

What angle would you expect to be formed by the C, O, H nuclei in an alcohol molecule? Explain.

Answer

These atoms form a bent arrangement as in

water. The oxygen bonds are formed by p orbitals. These orbitals are at 90° to each other in the free atom.

The student is not expected to know the exact value of the angle, about 105° .

Problem 9

It is possible to obtain from 6.1 g of the sweetener, saccharin, 10.3 g CO_2 , 1.50 g H_2O , 1.53 g NO_2 , and 2.13 g SO_2 . What is its empirical formula?

Answer

$$\frac{10.3 \text{ g } CO_2}{44 \text{ g/mole } CO_2} = 0.234 \text{ mole } CO_2 \quad \text{containing } 2.82 \text{ g C}$$

$$\frac{1.50 \text{ g } H_2O}{18 \text{ g/mole } H_2O} = 0.083 \text{ mole } H_2O \quad \text{containing } 0.16 \text{ g H}$$

$$\frac{1.53 \text{ g } NO_2}{46 \text{ g/mole } NO_2} = 0.0333 \text{ mole } NO_2 \quad \text{containing } 0.46 \text{ g N}$$

$$\frac{2.13 \text{ g } SO_2}{64 \text{ g/mole } SO_2} = 0.0333 \text{ mole } SO_2 \quad \text{containing } 1.06 \text{ g S}$$

sample accounted for 4.50 g

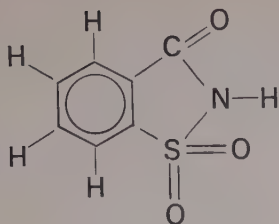
$$\text{Oxygen mass} = 6.1 - 4.5 = 1.6 \text{ g}$$

$$\frac{1.6 \text{ g O}}{16 \text{ g/mole of oxygen atoms}} = 0.100 \text{ mole O}$$

C	0.234	mole	or 7 relative amounts
H	0.163		5
O	0.100		3
N	0.0333		1
S	0.0333		1

Empirical formula $C_7H_5O_3NS$

This is also the molecular formula although the student has no way to know it. The structural formula given on the next page will be mentioned in Chapter 18 where the structure of the benzene ring will be discussed.

**Problem 10**

Burning 0.600 g of an alcohol obtained by processing petroleum gave 1.32 g CO_2 and 0.72 g H_2O . One mole of the alcohol weighs 60 grams. Determine the molecular and structural formulas. Are there two isomers of this alcohol?

Answer

$$\frac{1.32 \text{ g CO}_2}{44 \text{ g/mole CO}_2} = 0.030 \text{ mole CO}_2$$

containing 0.36 g C

$$\frac{0.72 \text{ g H}_2\text{O}}{18 \text{ g/mole H}_2\text{O}} = 0.040 \text{ mole H}_2\text{O}$$

containing 0.08 g H
sample accounted for 0.44 g

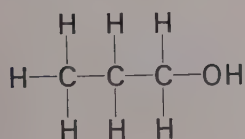
$$\text{Oxygen mass} = 0.600 - 0.44 = 0.16 \text{ g}$$

$$\frac{0.16 \text{ g O}}{16 \text{ g/mole of oxygen atoms}} = 0.010 \text{ mole O}$$

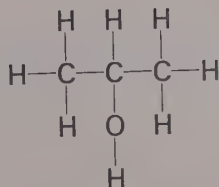
C	0.030 mole	or 3 relative amounts
H	0.080	8
O	0.010	1

Empirical formula $\text{C}_3\text{H}_8\text{O}$

The mass of the empirical formula equals 60 g which is the same as the molar mass given. The molecular formula is also $\text{C}_3\text{H}_8\text{O}$. Possible structural formulas for alcohols are



n-propanol



isopropanol

Problem 11

When 0.01 mole of an organic acid is dissolved in distilled water and titrated to phenolphthalein endpoint using 0.1 *M* NaOH solution, 200 ml of base solution was needed. How many ionizable hydrogen atoms are there in each molecule?

Answer

$$(0.1 \text{ mole OH}^-/\text{liter}) \left(\frac{200 \text{ ml}}{1000 \text{ ml/liter}} \right)$$

$$= 0.02 \text{ mole OH}^- \text{ used}$$

Each OH^- reacts with one H^+

$$\left(\frac{0.02 \text{ mole OH}^-}{0.01 \text{ mole compound}} \right) \left(\frac{1 \text{ H}^+}{1 \text{ OH}^-} \right)$$

$$= 2 \text{ moles H}^+/\text{mole compound}$$

Problem 12

Methyl sulfide, $\text{H}_3\text{C}-\text{S}-\text{CH}_3$, and ethyl mercaptan, $\text{CH}_3\text{CH}_2\text{SH}$, absorb light at different frequencies. Explain.

Answer

This case is similar to the ether-alcohol one. There are different bonding arrangements, therefore different electron environments. As a result, the spectra are different. The sulfide should have C—H stretching vibrations but no S—H vibrations. The mercaptan has both.

Problem 13

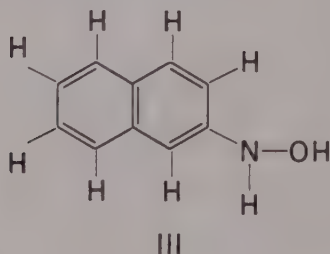
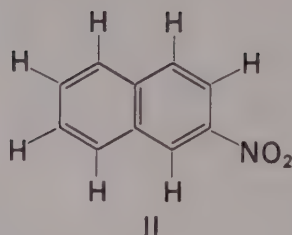
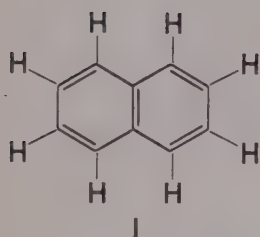
An isomer of the compound $\text{C}_4\text{H}_9\text{O}$ absorbs strongly at 9.5×10^{13} cycles/sec. Is this isomer an alcohol or an ether?

Answer

An alcohol. The 9.5×10^{13} frequency results from the stretching vibration of the O—H bond.

Problem 14

The following colorless solids all melt at 79–80°C. Indicate the types of bonds present in each (C—H, etc.) and describe how infrared spectra could be used to identify the compounds.

**Answer**

All three compounds have C—H and C—C bonds. However, compound II has C—N and N—O bonds while compound III has these and O—H and N—H. These different bonding arrangements would have different infrared frequencies. By using known compounds, the region for each type could be identified.

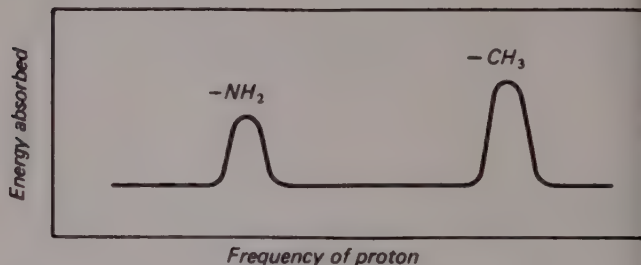
Problem 15

Draw a schematic NMR spectrum for methyl amine, CH_3NH_2 .

Answer

The amine has C—H and N—H bonds involving protons. The student can be expected to suggest two peaks, one for each type of proton. The first should be larger as there are more of such hydrogen atoms. The better students can decide the relative positions of the peaks as follows. In ethanol, where the proton is bonded to an atom with high electron attracting power, oxygen, the peak was to the left of the CH_3 peak. Nitrogen also has a strong attraction for electrons. There-

fore, the N—H peak can be expected on the left of the CH_3 peak.

**Problem 16**

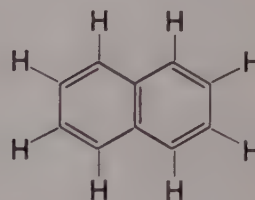
How many peaks do you predict for the NMR spectrum of acetic acid? Explain.

Answer

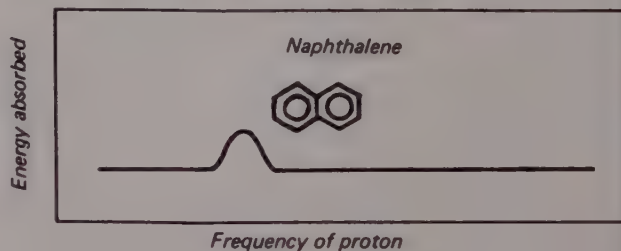
The hydrogen atoms in this compound are bonded either to carbon or oxygen so there should be two peaks.

Problem 17

Draw a schematic NMR spectrum for naphthalene.

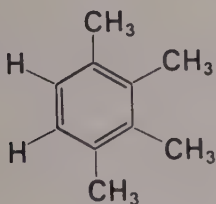
**Answer**

In this molecule, all the hydrogen atoms are bonded to carbon atoms in the ring structure. Hence we would expect one large peak.

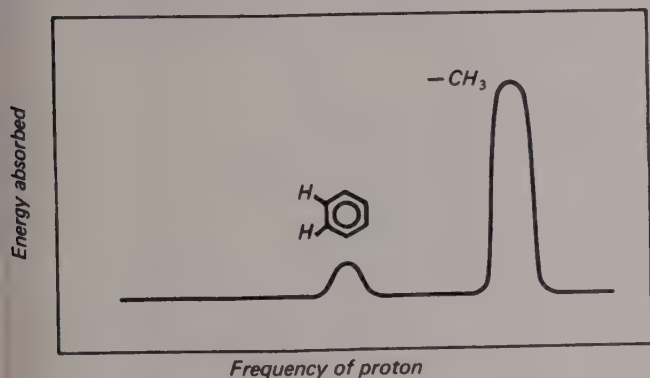


Problem 18

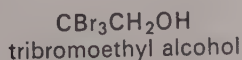
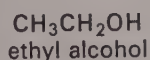
Draw a schematic NMR spectrum for 1,2,3,4-tetramethylbenzene.

**Answer**

The 12 CH_3 protons produce one large peak and the two protons bound to the ring produce a small peak.

**Problem 19**

Compare the formulas of ethyl and tribromoethyl alcohols. Indicate how their NMR spectra would be different. Use Figure 16-12.

**Answer**

Peak C in Textbook Figure 16-12 would be absent in the spectrum of tribromoethyl alcohol as there are no CH_3 protons.

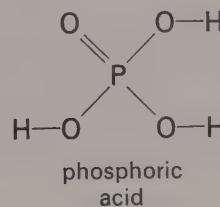
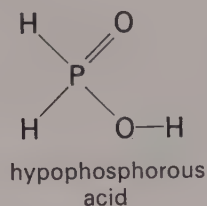
Problem 20

The NMR spectrum for hypophosphorous acid, H_3PO_2 , shows two peaks. The spectrum for phosphoric acid, H_3PO_4 , gives only one peak. Explain.

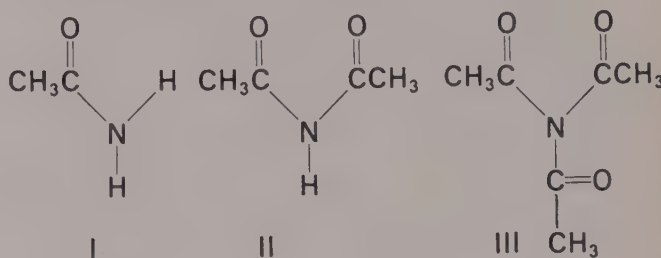
Answer

There must be two kinds of bonding arrangements

for the protons in H_3PO_2 and just one in H_3PO_4 . The structures, which the student is not asked to give, are

**Problem 21**

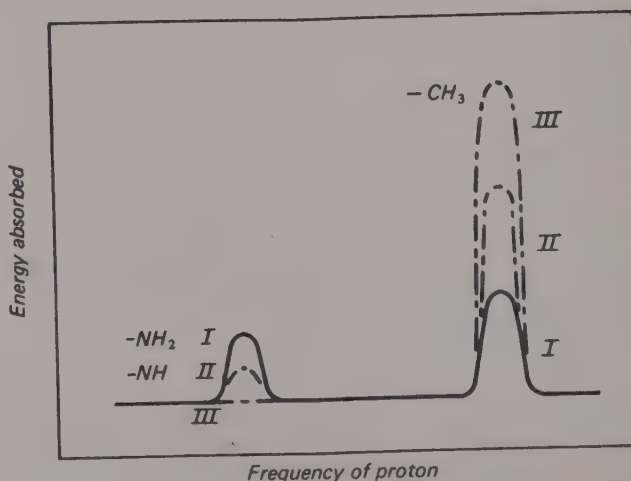
Three colorless compounds, all melting in the range $79-81^\circ\text{C}$, possess the following structures



Indicate, using schematic spectra, how NMR could help identify them.

Answer

The number of hydrogen atoms attached to nitrogen is 2, 1, or 0 in these compounds. This feature would show prominently in the NMR spectra. Some students may draw schematic spectra which should have the features shown below.



Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

There are several oxides of nitrogen. Careful analysis of one of these oxides shows that 30.0 grams of the compound contains 14.0 grams of nitrogen.

1. What is the empirical formula for this oxide of nitrogen?

Answer

$$30.0 \text{ g} - 14.0 \text{ g} = 16.0 \text{ g oxygen}$$

$$\frac{14.0 \text{ g nitrogen}}{14.0 \text{ g nitrogen/mole}}$$

$$= 1.00 \text{ mole nitrogen atoms}$$

$$\frac{16.0 \text{ g oxygen}}{16.0 \text{ g oxygen/mole}}$$

$$= 1.00 \text{ mole oxygen atoms}$$

The ratio is 1 atom of nitrogen per 1 atom of oxygen. Therefore the empirical formula is NO.

2. A 92.0 gram sample of another oxide of nitrogen contains 28.0 grams of nitrogen. What is the empirical formula for this oxide of nitrogen?

Answer

$$92.0 \text{ g} - 28.0 \text{ g} = 64.0 \text{ g oxygen}$$

$$\frac{28.0 \text{ g nitrogen}}{14.0 \text{ g nitrogen/mole}}$$

$$= 2.00 \text{ moles nitrogen atoms}$$

$$\frac{64.0 \text{ g oxygen}}{16.0 \text{ g oxygen/mole}}$$

$$= 4.00 \text{ moles oxygen atoms}$$

The ratio is 1 atom of nitrogen per 2 atoms

of oxygen. Therefore the empirical formula is NO_2 .

3. Two compounds are known that contain only phosphorus and chlorine. Accurate analysis shows that 68.7 grams of compound I contain 15.5 grams of phosphorus, whereas 104.0 grams of compound II contain 15.5 grams of P.

- (a) Find the mass of chlorine combined with 15.5 grams of phosphorus in each compound, and calculate the ratio of chlorine in compound I to that in compound II.
- (b) Compound I is PCl_3 . Decide whether compound II is P_2Cl_2 , P_2Cl_4 , or PCl_5 .

Answer

- (a) Compound I:

$$68.7 \text{ g} - 15.5 \text{ g} = 53.2 \text{ g Cl}$$

Compound II:

$$104.0 \text{ g} - 15.5 \text{ g} = 88.5 \text{ g Cl}$$

$$\frac{\text{Cl in I}}{\text{Cl in II}} = \frac{53.2}{88.5} = 0.6$$

- (b) Compound II is PCl_5 . Compute the following ratios of chlorine in compound I to chlorine in compound II, and compare to 0.6 in part (a).

$$\frac{\text{Cl}_3}{\text{Cl}_2} = \frac{3 \times 35.5}{2 \times 35.5} = \frac{3}{2} = 1.5$$

$$\frac{\text{Cl}_3}{\text{Cl}_4} = \frac{3 \times 35.5}{4 \times 35.5} = \frac{3}{4} = 0.75$$

$$\frac{\text{Cl}_3}{\text{Cl}_5} = \frac{3 \times 35.5}{5 \times 35.5} = \frac{3}{5} = 0.6$$

4. There have been some attempts to make inorganic "rubber" by reacting NH_4Cl and PCl_5 . One compound produced was found to contain P, N, and Cl only. A 0.390 g sample had 0.103 g P and 0.047 g N. What is the empirical formula?

SUGGESTED QUIZ QUESTIONS

Answer

$$\text{mass Cl} = 0.390 \text{ g} - 0.103 \text{ g} - 0.047 \text{ g} \\ = 0.240 \text{ g}$$

$$\frac{0.103 \text{ g P}}{31.0 \text{ g P/mole}} = 0.00332 \text{ mole P}$$

$$\frac{0.047 \text{ g N}}{14.0 \text{ g N/mole}} = 0.00336 \text{ mole N}$$

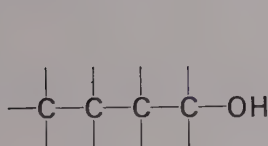
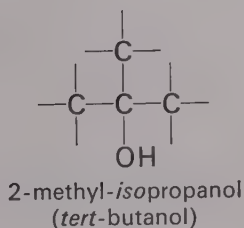
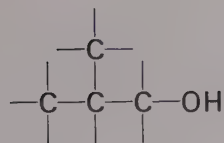
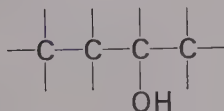
$$\frac{0.240 \text{ g Cl}}{35.5 \text{ g Cl/mole}} = 0.00675 \text{ mole Cl}$$

P	0.00332	1
N	0.00336	1
Cl	0.00675	2

The empirical formula is PNCl_2 .

5. Draw structural formulas of the isomers of butyl alcohol, $\text{C}_4\text{H}_9\text{OH}$.

Answer

*n*-butanol2-methyl-*isopropanol*
(*tert*-butanol)2-methyl-*n*-propanol*sec*-butanol

6. When 0.652 gram of a sample having an empirical formula CH_3O was vaporized at 200°C , and one atmosphere pressure, the volume occupied was 388 ml. This same volume was occupied by 0.280 gram of $\text{N}_2(\text{g})$ under the same conditions. What is the molecular formula of CH_3O ?

One mole of the sample when reacted with

Na metal, liberated (rather slowly) $\frac{1}{2}$ mole of hydrogen gas. Write the structural formula.

Answer

Equal volumes at identical conditions contain the same number of moles. Thus,

$$\frac{0.280 \text{ g N}_2}{28.0 \text{ g N}_2/\text{mole}} = 0.0100 \text{ mole N}_2$$

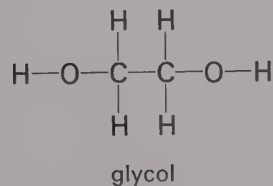
Thus 0.652 gram of unknown equals 0.0100 mole; therefore 65.2 grams are 1.00 mole. The formula must be some multiple of CH_3O . The corresponding masses of one mole are

CH_3O	31 g
$\text{C}_2\text{H}_6\text{O}_2$	62 g
$\text{C}_3\text{H}_9\text{O}_3$	93 g

Thus the molecular formula is $\text{C}_2\text{H}_6\text{O}_2$.

The structural formula follows from this fact:

One mole of unknown gives $\frac{1}{2}$ mole of H_2 , indicating that there is only one active hydrogen atom. The formula that best fits these data is



glycol

7. Eleven grams (11.0) of a compound containing only C, H, and O was found by analysis to give 22.0 g CO_2 and 9.0 g H_2O when burned completely. Calculate the empirical formula.

Answer

$$22.0 \text{ g CO}_2 \times \frac{1}{44.0 \text{ g/mole}} = 0.50 \text{ mole CO}_2$$

$$9.0 \text{ g H}_2\text{O} \times \frac{1}{18.0 \text{ g/mole}} = 0.50 \text{ mole H}_2\text{O}$$

Each mole of CO_2 contains one mole of C atoms, and each mole of H_2O contains two moles of H atoms.

$$0.50 \text{ mole } \text{CO}_2 \times \frac{1 \text{ mole C}}{\text{mole } \text{CO}_2} \times \frac{12 \text{ g C}}{\text{mole C}} = 6.0 \text{ g C}$$

$$0.50 \text{ mole } \text{H}_2\text{O} \times \frac{2 \text{ mole H}}{\text{mole } \text{H}_2\text{O}} \times \frac{1 \text{ g H}}{\text{mole H}} = 1.0 \text{ g H}$$

Oxygen must make up the rest of the 11.0 g sample.

$$11.0 - 6.0 - 1.0 = 4.0 \text{ g O}$$

$$4.0 \text{ g O} \times \frac{1}{16 \text{ g O/mole}} = 0.25 \text{ mole O}$$

The moles of each kind of atom are:

C	0.50	2
H	1.0	4
O	0.25	1

The empirical formula is $\text{C}_2\text{H}_4\text{O}$.

8. Most of the sunlight in the spectral region 2×10^{13} to 12×10^{13} cycles/sec fails to reach the earth's surface because the atmosphere is almost opaque in much of this region. Water vapor and carbon dioxide are the chemical substances that absorb most of this light. Describe the type of excitation accompanying the absorption of this light.

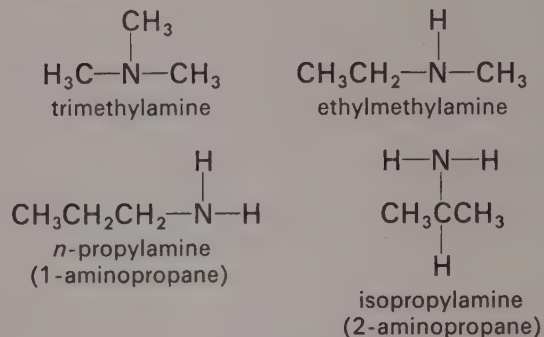
Answer

The region described is the infrared spectral region. Water and CO_2 absorb in this region, leading to excitation of vibrational motions.

Consider the empirical formula $\text{C}_3\text{H}_9\text{N}$ for Problems 9 and 10.

9. Draw structural formulas for at least three compounds fitting that relative composition and obeying normal bonding rules.

Answer

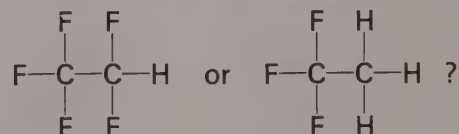


10. Describe in general terms how spectral data could help decide which isomer a pure sample was.

Answer

The student reply should contain some of these possibilities.

- The number of N—H bonds is different for several isomers. Infrared or NMR spectra could detect that fact.
 - There are several combinations of CH_3 , CH_2 , and CH groups. These groupings could be found by NMR or possibly infrared spectroscopy.
 - Solid samples of the isomers should give different diffraction patterns.
11. Would NMR spectra be useful in deciding whether a chemical reaction produced

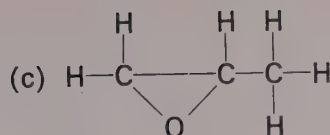
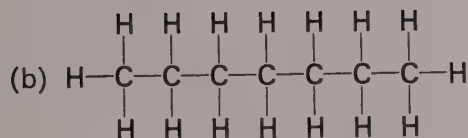
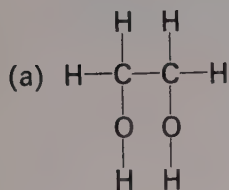


Explain.

Answer

There are a different number of H (or F) atoms and the protons occur in a different electron environment in the two compounds. Therefore we would expect the compounds to show peaks of different size (CF_3CH_3 larger) and at different resonance frequencies.

12. What infrared absorption frequencies would you expect for



Answer

(a) 8.7×10^{13} cycles/sec from the C—H stretching vibration.

9.5×10^{13} cycles/sec from the O—H stretching vibration.

(b) and (c) 8.7×10^{13} cycles/sec from the C—H stretching vibration.

Other modes of vibration would appear in the spectra, but the student has not been told of them.

Chemical Bonding in Gases, Liquids, and Solids



Intent and Approach

Chemical bonding is considered in detail: first for molecules in the gas phase, with attention to the polar character of bonds and how particular arrangements of such bonds lead to polar molecules. The basic principles that explain bonding between atoms in gaseous molecules are then applied to the more complicated situations presented by condensed phases. Our intent is to show how the ideas of valence orbital occupancy, ionization energy, and electron shar-

ing by nuclei can be used to draw a coherent picture of molecular solids, network solids, and metals.

One major purpose of Chapter 17 is to provide the student with a basis for understanding the properties of the various kinds of condensed phases and a basis for predicting which should be expected for a given chemical substance. Some of the types presented are molecular, network, metallic, ionic, and hydrogen-bonded solids.

Outline

Unsymmetric distribution of bonding electrons is a result of unequal attractive forces. Section 17-1 introduces polar bonds.

The spatial arrangement of bonds can yield a molecule with or without a dipole. Section 17-2 shows how such considerations help decide the shape of molecules.

van der Waals forces, caused by momentary dipoles, account for the attraction in molecular solids (17-3, 17-4).

When covalent bonds extend throughout the solid, network solids result (17-5).

Metals are formed when there is an excess of unfilled orbitals compared to the bonding

electrons available (17-6).

Closest-packing of spheres can occur in two ways (17-7). Most metals crystallize with the atoms in one of these arrangements.

Sections 17-8 and 17-9 offer explanations for the properties of metals and alloys.

Ionic solids receive attention in three sections. Section 17-10 treats their formation, 17-11 their structure, and 17-12 their solubility in water.

Hydrogen bonding is an important interaction. Section 17-13 indicates some features of this bond type.

Section 17-14 is a review.

New Concepts

1. Bonding electrons may be unsymmetrically distributed, giving a polar bond.
2. Molecules have shapes which often influence their properties.
3. Neutral, nonpolar molecules (and noble gas atoms) attract each other weakly. The forces are called van der Waals forces.
4. Covalent bonding accounts for the structure and properties of some solids.
5. Atoms with low ionization energy and empty orbitals form metals.
6. Compounds containing atoms with very different ionization energies usually form ionic solids.
7. A hydrogen atom bonded to oxygen, nitrogen, or fluorine can interact strongly with another atom. The interaction is called a hydrogen bond.

SCHEDULE AND RELATED MATERIAL

Suggested Time: 7 days

Text Section	Topic and Other Work	Exercises	Problems		
			Easy	Medium	Hard
	<i>Film:</i> Shapes and Polarities of Molecules				
17-1	Polar Molecules		2	1, 3, 4	5-8
17-2	Molecular Architecture	1, 2	9	10	11
	<i>Film:</i> Chemical Bonding*				
17-3	van der Waals Forces			12	
17-4	Molecular Solids	3-5			
17-5	Network Solids	6-8		13	
17-6	Metallic Solids			14, 15	
	Expt. 38. Packing in Crystals				
17-7	Crystal Structure of Metals	9, 10			
17-8	Explanation of Metallic Properties				
17-9	Alloys				
17-10	Ionic Solids			16-19	20, 21
17-11	Structure of Ionic Solids				
17-12	Solubility of Electrolytes in Water				
17-13	Hydrogen Bonds		22		23
17-14	Review				

* Suggested in Chapter 10. Repeat only at your choice.

Development

Introduction

The extreme range of properties represented in the condensed phases of pure lithium, pure flu-

orine, and lithium fluoride is used to encourage consideration of the kinds of bonding found in condensed phases. Emphasize that the principles

developed in Chapters 7 (ionization energy), 9 and 10 (valence orbital occupancy, electron sharing, charge separation) will provide a basis for understanding these systems. Notice that this chapter centers primarily on the properties of solids. Liquids are much more complicated.

Film, SHAPES AND POLARITIES OF MOLECULES,

fits here. See p. 352 for summary.

MOLECULES IN THE GAS PHASE

17-1 Polar Molecules

After explaining the underlying idea that *all* chemical bonds are formed for the same reason—a sharing of electrons between two nuclei—introduce the concept that the electrons need not be shared equally. The attraction an atom displays toward electrons varies from atom to atom. Hence the sharing may be more effective (give a lower energy) if it favors one atom somewhat more than the other.

In a qualitative way, ionization energy can be used as a basis for discussing the unequal sharing tendency. The *difference* in ionization energy between two bonded atoms is the influential factor. When this difference is very small or zero, the electrons are shared equally. Such a bond is called covalent. When this difference is very large, the electrons are strongly pulled toward one of the atoms, and the bond is called ionic. But among chemical bonds we can expect to find all magnitudes of differences. Hence we can expect to find a continuous range of bond types from covalent to ionic. By no means is it desirable to attempt to classify all bonds as one or the other, covalent or ionic. We must base our discussion of bonding on the recognition of a continuous range of bond types.

Note that a strict use of ionization energy for hydrogen will lead to incorrect predictions. Hydrogen behaves as though its ionization energy is about 200 kcal/mole instead of the measured value, 313.6 kcal/mole.

The dipole moment is introduced somewhat gingerly. The idea of “moment” is never introduced, the term electric dipole being used exclusively. Experiments do not reveal the amount of charge or of separation; they only show the product of charge times distance. The “moment” idea is difficult under any circumstances and is even more confusing when there is no basis for deciding how far apart the separated charges really are. In this first treatment, it is sufficient to speak of the electric dipole and to picture it as centered on the atomic centers. The important idea to emphasize is that, as ionic bond character increases, charge separation (hence, electric dipole) increases.

17-2 Molecular Architecture: The Shapes of the Second-Row Fluoride Molecules

In a molecule more complicated than a diatomic molecule, there must be two or more chemical bonds. Each of these bonds can have associated with it some ionic character (depending upon the atoms connected); hence it is reasonable to attribute an electric dipole to each bond. The total molecular electric dipole can then be discussed in terms of these individual “bond dipoles.” This is regularly done because a significant understanding of molecular dipoles results from making simple vector sums of hypothetical “bond dipoles.”

According to this view, two factors determine the molecular dipole: the degree of ionic character of individual bonds and the geometrical way in which the bond dipoles are oriented relative to each other. For example, the bonds in both F_2O and BeF_2 show some ionic character, but the difference in ionization energies indicates that the bonds in BeF_2 are more ionic. The molecular dipole, however, is the vector or geometrical sum of two bond dipoles in each molecule. In BeF_2 , the linear arrangement results in exact cancellation and in a net zero molecular dipole (as shown in Textbook Figure 17-1, p. 330). For F_2O , the bent structure leaves a net molecular dipole directed along the bisector of the angle formed by the two bonds (as shown

DEVELOPMENT

in Textbook Figure 17-6, p. 334).

The more complicated examples, BF_3 and CF_4 , involve the same principles used in the F_2O - BeF_2 comparison. Discussion of BF_3 may be aided by using a travel analogy. The result of two straight-line airplane flights can be likened to a vector sum. For BF_3 , the succession of three flights, properly directed, brings the traveler back to his starting place. It is probably not worthwhile trying to apply such a travel analogy to a non-planar molecule (though it can be done).

This section also provides a basis for predicting qualitatively the shapes of molecules. Treat the correlations as empiricisms, emphasizing that they are useful because they work. We do not wish to say that H_2O *must* be a bent molecule *because* of the orbitals used in its bonding. Instead we note the correlation between the use of two p orbitals in the bonding and the resulting bent structure. From this correlation we can predict that a molecule will be bent if the electron configuration of the central atom provides only these two orbitals for bonding. The bonding in the molecule is then called p^2 , a convenient name because it tells us not only which type of orbitals are involved but the molecular structure as well.

The perpendicularity of p orbitals of the oxygen atom provides a reasonable basis for discussing bent structures for H_2O and F_2O (and pyramidal structures for NH_3 and NF_3). It does not prove that the structures must be bent (or pyramidal); indeed, the structures can be explained in quite another way (see the *Background Discussion*).

The empiricism involved in discussing molecular architecture is most important in treating the tetrahedral bonding of carbon and the planar trigonal bonding of boron. Here again we find that an atom can bond to four other atoms when one s and three p orbitals are available. When this is the case, we find that these bonds are tetrahedrally oriented. Hence we can associate with confidence the label sp^3 (indicating that these four orbitals are half-filled) and the tetrahedral geometry. This is true for unsymmetrical compounds, such as CH_3F , as well as for CH_4 and CF_4 . As you know, the structures of many

organic molecules are explained by repetition of this simple arrangement.

A set of Cartesian coordinates is helpful for demonstrating the spatial arrangements of the bonds. Two balloons tied together make a convincing p orbital, and two or three of these pairs can be used together to illustrate p^2 and p^3 orbital arrangements. Ball-and-stick models of NF_3 , CF_4 , and BF_3 are more helpful than chalk-board drawings.

Film, CHEMICAL BONDING,

fits here. See p. 177 for summary.

Note this film was also recommended for use after Section 10-2. Repeat only at your choice.

BONDING IN LIQUIDS AND SOLIDS

17-3 van der Waals Forces

17-4 Molecular Solids: Argon, Chlorine, Sulfur, and Phosphorus

Just because charge separations (bond dipoles) may occur does not mean they must occur. The C—H bond, for example, involves a very small electric bond dipole. Even for molecules involving substantial bond dipoles, molecular symmetry can cause cancellations that result in a zero molecular dipole. Molecules having zero molecular dipoles attract each other with the same weak van der Waals forces that account for liquefaction and solidification of the noble gases and of such elements as F_2 , Cl_2 , P_4 , and S_8 . Thus we find an explanation for the properties of such molecular compounds as CF_4 , CH_4 , CCl_4 , C_2Cl_6 , BF_3 , CO_2 , etc. Because the forces between molecules are so weak, many properties of these substances remain virtually unchanged as the molecules pass from gas to liquid to solid state. Therefore, such substances are called molecular solids.

The halogens, nitrogen, sulfur, and phosphorus form molecules in which covalent bonding capacity is satisfied. Without additional bonding

capacity, molecules such as F_2 , N_2 , P_4 , and S_8 behave like noble gas atoms. The inter-molecular forces between molecules are very weak—much weaker than the forces holding the atoms together in each molecule. These weak forces are called van der Waals forces.

To explore these forces, let us consider the interaction between two sulfur molecules (formula S_8) (see Textbook Figure 17-9, p. 337). Let's call the two molecules M_1 and M_2 . As M_1 is brought close to M_2 , electrons attached to the sulfur nuclei in M_1 are simultaneously attracted to the sulfur nuclei of M_2 . The case is like that pictured for two helium atoms in Section 10-2, p. 175. The electrons of M_1 cannot occupy the valence orbitals of the atoms of M_2 because the valence orbitals of every atom in M_2 are occupied by an electron pair. The same is true for the interaction between the electrons of M_2 and the nuclei of M_1 . Since the two molecules cannot approach closely, the attractions are much weaker than they are when electrons simultaneously occupy valence orbitals of each atom. The valence electrons of M_1 can be shared with M_2 only through extra-valence orbitals of M_2 (and *vice versa*).

Thus the discussion of van der Waals forces is built upon the discussion of the interaction of two helium atoms in Section 10-2. Notice that this is but one of the contributions to van der Waals forces. Other contributions are present when molecular dipoles exist.

17-5 Network Solids: Silicon and Carbon

The normal bonding of a carbon atom gives a tetrahedral bond orientation, as in methane. The spatial arrangement around the carbon would not be expected to change if each of the four hydrogen atoms in methane were replaced by a carbon atom. The central carbon would bond to each of the four adjacent carbons by sharing electrons, just as do the two fluorine atoms in F_2 . When four carbons share electrons with a central carbon, four normal covalent bonds result. But

the four peripheral carbon atoms have residual bonding capacity. Thus each of these must also have four neighbors, each neighbor requiring three additional carbon atoms to join the aggregate of atoms. This must be continued *ad infinitum*, building up an infinite network held together by normal, covalent bonds.

Recall that the existence of network solids requires only the repeated application of ideas encountered in previous chapters. The orbital occupancy, bonding capability, and angular distribution of the bonds determine the molecular structure in the same way for a diatomic molecule such as F_2 , for an eight-atom molecule like S_8 , and for an "infinite molecule" like a diamond crystal.

The silicates furnish another excellent example; first, because they are so abundant and, second, because the network types are so obviously responsible for an interesting range of macroscopic mineral properties (Figure 17-15, p. 341).

17-6 Metallic Solids: Aluminum, Magnesium, and Sodium

The properties of metals identify a new bonding situation. Yet the existence of metals can also be explained quite simply on the basis of the concepts introduced in Chapters 15 and 16. In metals the electrons are shared among atoms having very low ionization energies and vacant valence orbitals.

Emphasize that most of the elements are metallic. The common properties (electrical conductivity, thermal conductivity, luster, malleability, ductility, etc.) dictate a similar explanation for all. Since metals are characterized by low ionization energies and vacant valence orbitals, a natural model would consist of regularly spaced positive nuclei that have "surrendered" their valence electrons to a communal sharing. The positive nuclei would be immersed in a sea of mobile, free-moving electrons. With such a model, the characteristic properties of metals and the trends shown by their properties are readily explained.

DEVELOPMENT

**Expt. 38, THE PACKING OF ATOMS
IN CRYSTALS,**

fits here. See p. 216 in the Laboratory Guide.

17-7 Crystal Structures of Metals

Because the atoms must share the mobile electrons in several valence orbitals, we find that orbital directionality is no longer so important in bonding. Instead the atoms merely seek a packing that places them as close together as possible. Hence the crystal structures can be discussed in terms of the ways in which spherical objects can be packed together. The closest packing arrangements are those found most commonly among metallic crystals. These are explored with models in Expt. 38.

Note that this experiment is unusually important because the spatial relations are difficult to see without the actual spheres in hand.

17-8 An Explanation for Metallic Properties**17-9 Alloys**

New principles are not needed in discussing metallic alloys. The ease of forming alloys is readily explained within the metallic model we have used. Since the bonding between neighbors is diffuse—through the highly mobile “electron sea”—impurity substitutions can occur without serious disturbance to the crystal bonding. If the impurity atoms tend to form rigid and localized bonds (as does carbon, for example), then metallic properties are sacrificed somewhat. The result is that we have great control over such metallic properties as electrical conductivity, tensile strength, hardness, brittleness, melting temperature, etc., through alloy formation.

17-10 Ionic Solids

This section mainly reinforces Section 10-1. See p. 174.

17-11 Structure of Ionic Solids

The several kinds of ions in a crystal of ionic solid will not all be the same size. Hence closest-packing in the exact sense of Experiment 38 is not possible. Further, the ionic charge causes like ions to repel each other so that usually they will *not* be touching. As a result, ionic crystals form a number of arrangements which have three features in common. They are:

explained by assuming ions are in contact,
positive and negative charges alternate in some
regular way,
the anions are usually larger than the cations.

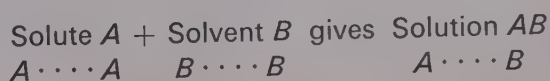
The *Background Discussion* gives a fuller treatment, p. 353.

17-12 Solubility of Electrolytes in Water

There is no doubt that polarity has an influence on solubility. It is not the only factor, however, and, if considered alone, can lead to erroneous statements. One such statement is “like dissolves like.” Although this rule of thumb does have some use *for an experienced person*, it is not suitable for a beginner. Much of the beginner’s limited experience is in conflict with the rule, which in turn is too limited.

Consider, for example, the ways in which NaCl and AgCl are alike. Yet how different are their solubilities in water! On the other hand, two quite soluble substances, salt and sugar, are decidedly unlike. In none of the three—NaCl, AgCl, or sugar—is there any obvious resemblance to the solvent, water.

Finally, the rule is frequently applied in a circular fashion: “like dissolves like”; like things are those which dissolve in the same solvent. A better way is to speak of the summation of energy and randomness effects required to break up the interactions between molecules of the two pure compounds and to form the interactions present in the solution. We can show this in terms of the general reaction



The dotted lines represent the interactions. There are now four possible cases, shown in outline form below.

Solute	Solvent	$A \cdots A$	$B \cdots B$	$A \cdots B$
Nonpolar	nonpolar	weak	weak	weak, not much change for solute or solvent; solubility can be high
Nonpolar	polar	weak	strong	weak, difficult to break up $B \cdots B$; solubility probably low
Polar	nonpolar	strong	weak	weak, difficult to break up $A \cdots A$; solubility probably low
Polar	polar	strong	strong	strong, not much change for solute or solvent; solubility can be high

You will notice the cautious comments about solubility. This is necessary because other factors such as entropy changes and hydrogen bonding might be acting in opposition to the interactions shown. Perhaps a more positive way to put the conclusions in the table is to say, for the first and last examples, that the polar properties are appropriate for good solubility. The reverse is true for examples 2 and 3. The final solubility achieved is the sum of this and other influences.

Striking effects of such molecular dipoles appear in the dielectric and solvent properties of liquids. The high dielectric constant of water is attributable to the high molecular dipole of this compact molecule. The most important single consequence is the dissolution of such substances as NaCl and HCl in water to yield solutions containing ions. The great stability of ionic solids is shown by their characteristically high

melting temperatures. Yet sodium chloride dissolves readily in water, showing that ions in water are also extremely stable. The explanation is found in the attractive interactions between the molecular dipoles of water and the ionic charges. The arrangement of the water molecules around a positive ion can be represented in terms of dipoles, as shown in Figure 17-25, p. 349.

17-13 The Hydrogen Bond

This section amplifies Section 10-7. Now the polar character of the bonds can be mentioned and used as a reason for the principal occurrence when hydrogen is bonded to oxygen, nitrogen, or fluorine. Highly electronegative atoms are needed to give the hydrogen sufficient "acidity."

17-14 Review

Supplementary Material

Films

SHAPES AND POLARITIES OF MOLECULES

A CHEM Study film

Running Time: 18 minutes

This film was made with the collaboration of Professor David Dows, University of Southern California, Los Angeles. Observations of electrical effects lead to the concept of electrical polarity. There are two types of results for covalent substances: some show very marked interactions with electric charges, whereas others give little effect. A model is developed that is based on considerations of bond polarity and molecular symmetry

which correlate the electrical effects and their change as temperature is varied. The molecular dipole model is extended to explain differences in solubility, conductivity, and chemical reactivity.

CHEMICAL BONDING

See p. 177.

"Film Strips on Molecular Models," J. A. Campbell, Encyclopaedia Britannica Series (seven film strips available), 1960.

Available from Encyclopaedia Britannica Films
1150 Wilmette Avenue
Wilmette, Illinois

Background Discussion

Introduction

In the present discussion, we attempt to present a brief systematic view of the interactions that hold matter in condensed phases. This topic is a very large one, and our discussion cannot be complete. We shall indicate the directions in which are found useful explanations for each of the various types of interaction, but we shall not be able to follow any of these paths very far.

In the development of chemistry, it has become convenient to identify the following types of interactions in solids and liquids:

- (1) covalent bonding,
- (2) van der Waals interactions,
- (3) metallic bonding,
- (4) ionic bonding,
- (5) hydrogen bonding.

All these interactions are ultimately accounted for by the simultaneous movement of electrons near two or more nuclei. In spite of this common cause, these interactions are distinguished because the properties of a system are influenced markedly by orbital occupancy, ionization energy, and charge distribution. We shall see how these three factors provide a coherent picture of the five types of interactions we have listed.

Solids and Liquids Distinguished

Before we consider in detail how the condensed states of matter are held together, it will be useful to distinguish between solids and liquids, on both a macroscopic and a microscopic scale. On a macroscopic scale such a distinction is easy and familiar. *A solid retains its shape regardless of the shape of the container, whereas a liquid tends to assume—at least to the extent that its volume allows—the shape of the confining volume.*

On a microscopic scale there are two distinctions that can be considered. The first relates to mobility of the constituent particles (atoms or molecules), and the second relates to order.

In solids the nearest neighbor particles (atoms or molecules) tend to remain in fixed relative positions over long time periods. In liquids, the nearest neighbor particles are constantly changing.* A given atom (or molecule) may migrate from one location to another while the number of nearest neighbors to a given atom (or molecule) remains constant, on the average, due to compensating migration of other atoms or molecules.

Another way in which solids and liquids can be contrasted on a microscopic scale is in relation to long distance order. Long distance order or repetitious spatial arrangement is not present in liquids. In some solids, called crystals, it is present; in others, called glasses, it is not. Let us consider crystals first.

A crystalline solid can be described as an orderly array of repeating units in space. The entire crystal can be "generated" merely by specifying the positions of a small number of atoms and some rules by which this unit is moved through space in regular increments. This small number of atoms is called a unit cell. In some crystals the rules for moving the unit cell are merely to slide (translate) it along the three Cartesian coordinate axes. In other crystals, the axes must be taken at angles other than 90°. In some crystals, the unit cell must be translated and turned. But in all cases, the unit cell is repeated again and again throughout the macroscopic dimensions of the crystal. A crystalline solid consists of an arrangement of atoms with this type of long range order. In contrast, a glass lacks this definite repeating order. It meets the macroscopic criterion of solids—it maintains shape—as well as the diffusion criterion—diffusion is often negligible in a glass. Nevertheless, the spatial arrangements are disordered, like those in liquid. In fact, a reasonable

* Diffusion within a solid is encompassed in this statement through the arbitrary specification "long time periods" For our purposes, we mean that diffusional movement can normally be neglected during experimentally significant time intervals (seconds, minutes, hours).

argument can be made for defining a glass as a limiting case of a liquid of very high viscosity. The viscosity of glycerin, for example, increases as temperature is lowered. The temperature at which it is considered to become a glass is difficult to ascertain and is, in fact, rather arbitrary. Ultimately, the classification of a glass as a "solid without long range order" or as a "liquid with extremely high viscosity" is a matter of convenience, and need not divert us further. Henceforth, we shall ignore the glassy state and shall interpret a solid as a condensed phase of matter possessing long range order, and a liquid as a condensed phase of matter without long range order.

Covalent Bonding in Network Solids

Whether a chunk of a covalently bonded crystal be called a network solid or a molecule is a matter of semantics dictated by convenience. Apparently the interactions that hold the carbon atoms together in diamond are the same as those that hold the four carbon atoms to the central carbon atom in a highly branched hydrocarbon such as $\text{C}(\text{CH}_3)_4$ (neopentane), in terms of both energy and bond orientation. The requirement that a molecule contain only a limited number of atoms is purely a matter of convenience (readily abandoned when desired, as it is in discussing the so-called "macromolecules," such as proteins). The important thing to stress is that the ideas already developed for gaseous molecules—the nature of chemical bonds, the number per atom, and their spatial arrangements—suffice for an understanding of the existence of network solids.

van der Waals Interactions

The principles we have developed to explain chemical bonding also aid us in seeing the origin of van der Waals interactions between atoms not held together by a chemical bond. The very general explanation of bonding explains that these forces, too, must arise because electrons are simultaneously near two nuclei. However, each valence orbital can hold but two electrons.

If these valence orbitals are all fully occupied, then the nuclei of nonbonded atoms must remain at relatively large separations and the interactions will be weak. In terms of orbitals, only extra-valence orbitals are accessible for electron sharing. The binding of an electron in an extra-valence orbital is quite weak.

With this general view of why atoms or molecules that have no empty bonding orbitals still display residual but very weak attractions, we can proceed to examine more closely the classifications that are convenient among van der Waals interactions. We shall consider only two types, London and dipole-dipole interactions.

LONDON INTERACTIONS

The forces that hold noble gas atoms together in the liquid and solid states (as well as symmetrical molecules like methane, CH_4) were explained by F. London. The London theory recognizes that the electron-electron repulsion between, for example, two helium atoms can be lessened if the electron movements correlate so as to keep the electrons apart. The electrons on one atom apparently spend as much time as possible between the two nuclei when the electrons of the second atom happen to be in some other region of space.

Mathematically, this situation can be likened to the interaction of two dipoles. An electron and the nucleus of the first atom are thought of as an "instantaneous electric dipole"; an electron and the nucleus of the second atom as another "instantaneous electric dipole." Energetically, these two dipoles seek an alignment in which opposite charges are close together. The result is as pictured in Figure 17-1; the electrons move with preference to energetically favorable arrangements like 1 and 2, while discriminating against unfavorable arrangements like 3 and 4. In each picture, the dominant intermolecular interaction is shown by broken lines. The London scheme permits a formulation of the statistical average of the net interaction. It is found to be attractive, and depends upon the internuclear distance as r^{-6} .

BACKGROUND DISCUSSION

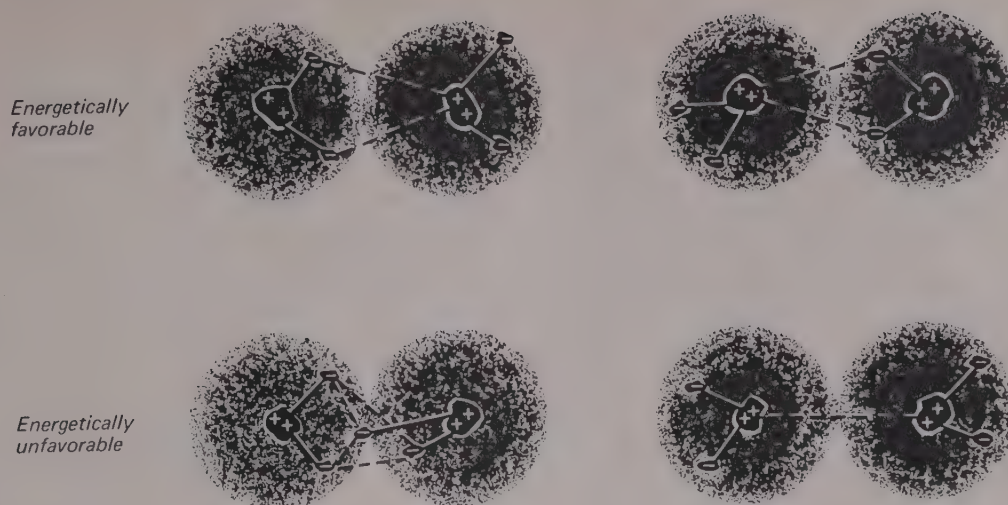


FIGURE 17-1

Favorable and unfavorable positions of electrons as helium atoms approach.

DIPOLE-DIPOLE INTERACTIONS

Molecules possessing nonzero electric dipoles interact more strongly than is accounted for by the London treatment. In certain ways, the problem is analogous to the "instantaneous dipole" interaction just described. This additional interaction also depends upon the distance as r^{-6} . Its magnitude depends upon the dipole moment very sensitively—as μ^4 for identical molecules—

and can be quite large if μ is appreciable! (For different molecules, A and B , the dependence is $\mu_A^2 \mu_B^2$.) Table 17-1 shows the calculated interactions due to dipole-dipole interactions and London interactions for a series of molecular species, all considered at 5.0 Å separation to provide a common basis. The trend in the results parallels that shown by the heats of vaporization.

TABLE 17-1

Calculated Intermolecular Interactions (All Calculations at 5.0 Å)

Molecule	Dipole Strength (Debyes)	Calculated Energy Due To		Sum	$\Delta H_{\text{vap'n}}$ (kcal/mole)
		London Forces	Dipole-dipole		
He	0	0.7	0	0.7	0.02
Ar	0	42	0	42	1.6
CO	0.12	66	0.003	66	1.4
HCl*	1.03	112	17	129	3.9
NH ₃ *	1.5	81	75	156	5.6
H ₂ O*	1.84	38	172	210	9.4

* Hydrogen bonding present.

Metallic Bonding

Metallic properties are found for the condensed phases of elements having the following properties:

low ionization energies;
vacant valence orbitals;
few valence electrons (relative to the number of valence orbitals).

We explain the existence of metals in terms of these three factors as follows. Under these conditions, the atoms cluster together as closely as possible so as to completely occupy the empty valence orbitals with the few valence electrons available. The combination of low ionization energy and many available orbitals yields an environment in which valence electrons are not localized in a particular region between two atoms, and thus do not form a single specific bond. Instead, they move freely about the central atom within the many available orbitals in such a way that they contribute to the bonding of several nearest neighbors. This free movement of the valence electrons accounts for the high electrical and thermal conductivities of metals.

There seems little question that low ionization energy plays a role in fixing metallic properties. For example, it is an empirical fact that all of the elements with distinctly metallic properties have first ionization energy below 250 kcal/mole. That the first ionization energy is by no means the only factor fixing metallic properties is readily

seen by comparing electrical conductivities (the most characteristic metallic property) to ionization energy.* Table 17-2 lists the fifteen elements having highest electrical conductivity in order of decreasing conductivity. The fourth column lists the first ionization energies. The absence of correlation is obvious. The lowest ionization energy among these elements is that of potassium (100 kcal/mole), which is next to last in electrical conductivity. Gold, which has one of the highest ionization energies, is the third best conductor among all the elements.

On the other hand, Table 17-2 suggests that whatever does cause high electrical conductivity also causes high thermal conductivity. Figure 17-2 shows a plot of these data. The correlation is clear at the higher values, and it is explained in terms of the contribution by the mobile electrons (which cause high electrical conductivity) to the thermal conductivity. Of

* The ionization energy *does* correlate with chemical properties of the metallic elements when they are *not* in the metallic state (e.g., acid-base properties).

TABLE 17-2
First Ionization Energy, Electrical and Thermal Conductivity
of the Fifteen "Most Metallic" Elements

Element	Electrical Conductivity (microhm-cm) ⁻¹	Thermal Conductivity (cal/cm-sec-deg)	First Ionization Energy (kcal/mole)
Ag	0.63	1.01	175
Cu	0.60	0.99	178
Au	0.46	0.70	213
Al	0.38	0.50	138
Ca	0.29	0.3	141
Na	0.24	0.32	118
Mg	0.22	0.38	176
Rh	0.22	0.21	177
Mo	0.19	0.35	170
Ir	0.19	0.14	212
W	0.18	0.4	184
Be	0.17	0.38	215
Zn	0.17	0.27	216
K	0.16	0.23	100
Co	0.16	0.16	182

BACKGROUND DISCUSSION

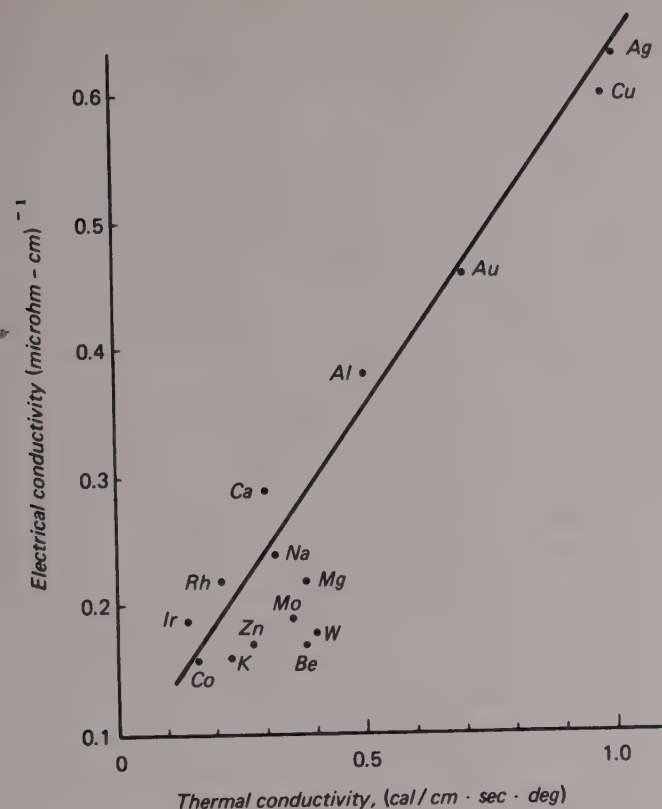


FIGURE 17-2

Relation between electrical and thermal conductivity.

course, a significant amount of the thermal conductivity that exists in certain solids (for example, sulfur) does *not* depend upon mobile electrons.

The Fermi Gas Model of Metals

The most elementary theory of metallic properties is based upon the calculated properties of a gas consisting of electrons confined within the crystal but free to move without restraint. It is assumed that these electrons do not interact either with the nuclei or with each other. Surprisingly, this simple model, called the Fermi Gas model, is remarkably successful in explaining many properties of metals. For example, classical theories of the heat capacity of metals predicted that the conduction electrons, if completely free, should contribute much more to the heat capacity than is found experimentally. Yet the Fermi Gas model explains the high conductivity without requiring a large contribution

to the heat capacity by the electrons. There are other successes, too, such as the agreement between the model and experiment in predicting that the electromotive force generated by a thermocouple should depend upon the square of the temperature of the bimetallic junction.

How this model gives rise to these predictions can be indicated only qualitatively here. The model gives the electrons only kinetic energy, since all potential energy interactions are ignored. A set of energy levels is generated, as in the hydrogen atom, but they almost form a continuum. Each energy level corresponds to a particular electron velocity in a particular direction. Corresponding to each energy level that designates electron movement in, for instance, a north-to-south direction in the crystal, there is another energy level that designates electron movement in the opposite direction, south-to-north. The Pauli Principle is assumed to apply, therefore only two electrons can occupy a given energy state. An enormous number of states is needed to accommodate all the valence electrons in a macroscopic crystal. For example, if the crystal contains one mole of sodium atoms, it contains 6×10^{23} valence electrons. Thus at absolute zero, 3×10^{23} energy states would be occupied.

Let us first examine how this model explains electrical conductivity. With no external electric field, electrons occupy as many of the north-to-south levels as they do the south-to-north levels. No net electron movement results. When an appropriate electric field is applied, however, the north-to-south moving electrons are moving "downhill" energetically, and the south-to-north moving electrons are moving "uphill." That is, all the north-to-south levels are lowered slightly, and the others are raised slightly. Some of the electrons spill over from the south-to-north levels into the lower-energy north-to-south levels. With more electrons having kinetic energy carrying them toward the south than there are electrons moving toward the north, conductivity results. The ease of obtaining this type of conductivity arises because the levels in this model are so closely spaced that only a small electric

field is needed to get a net current. Since the model neglects all interactions with the atoms, the moving electrons cannot transfer energy to the lattice, and the model predicts zero electrical resistance.

The Band Theory: Bloch's Model

Felix Bloch made a significant improvement on the Fermi Gas model by introducing a periodic potential function to represent the effect of the positive nuclei in the crystal lattice. The Bloch model retained the desirable features of the Fermi Gas model and added a new facet. The addition of the periodic potential causes the practically continuous set of energy levels to break up into separate sets of practically continuous energy levels *with forbidden energies between the sets*. Thus arose the band theory of the energy levels of solids. The beauty of this new feature is that it provides an explanation for semiconductor behavior as well as metallic behavior. If the number of electrons in an element is such that one of the sets of energy levels is only partially filled, then the uppermost electrons behave as do electrons in a Fermi Gas. Metallic properties result. But if the number of electrons per atom is such that one of the sets of energy levels is exactly filled, right up to the top level of a band (e.g., for Si or Ge), then the next unoccupied levels are separated by a forbidden energy zone. A nonconductor (dielectric) results. Then the electrical properties are not at all like those of metals. In fact the electrical conductivities can be completely dominated by the electron occupancy of "perturbed" energy levels, the perturbations being caused by minute concentrations of impurities. This is the type of phenomenon that gives rise to transistor action. The language used in the Textbook—"an array of positive ions . . . immersed in a 'sea' of mobile electrons" (p. 342)—is intended to suggest the Bloch model of solids.

Bond Angles

Two relatively popular models are used to explain the bond angles formed in polyatomic mole-

cules. One is based upon the angular distributions of the hydrogen atom orbitals; it is called the "hybridization" model. The other model is based upon the electrostatic repulsions among the bonding and nonbonding valence electrons. We shall call it the "electrostatic" model. The discussion given in the Textbook is, deliberately, neither of these, though it is closer to the hybridization model. Either model furnishes a basis for understanding the qualitative aspects of molecular structure (linear or bent? planar or nonplanar? etc.). Both are ambiguous in explaining variations among bond angles for molecules with similar electron configurations. At this stage in the development of these models, an empirical view of bond angles seems most appropriate. Such a view is presented in the Textbook.

There is method in our choice of an empirical treatment based on the hydrogen atom orbitals. It permits the interested student to become familiar with the hybrid orbital notation, since he is certain to encounter it in his outside reading.

The Hybridization Model

In this model, the angular distributions of the hydrogen atom orbitals are presumed to persist in many-electron atoms and to be influential in determining the angles between bonds formed by a central atom. "Hybridization" is a term intended to indicate that when bonds having different types of orbitals are formed, the angular properties are to be explained on the assumption that some "mixing" of the different orbital types occurs to form "hybrid orbitals." Thus if an *s* and a *p* orbital are available for bonding, two bonds will form at angles appropriate to two "hybrid orbitals," each of which has part *s* and part *p* character. In this fashion, an explanation is framed for the empirical observation that two identical bonds are formed by an atom having an *s* and a *p* orbital available for bonding, though two different types of bonds might have been expected. A systematic movement across the Periodic Table displays the argument.

FLUORINE

The halogens have but one bonding orbital

BACKGROUND DISCUSSION

and do not raise the question of bond angle.

OXYGEN

The oxygen family has the valence orbital electron configuration $ns^2np_x^2np_y^1np_z^1$. The two bonding orbitals, p_y and p_z , are directed at right angles, and lead to an expected 90° bond angle. We do not need to invoke the hybridization ideal to explain the bonding of oxygen. Experimentally the data for the oxygen family compounds (shown in Table 17-3) are qualitatively compatible with this proposal. The hydride bond angles are in the range 104.5° to 90° . A convenient explanation of the angles greater than 90° is furnished by assuming that the bonding electrons of the peripheral atoms repel each other. This effect should decrease as the central atom becomes larger, a comfortable explanation of the large reduction of bond angle between H_2O and H_2S and the very slight further reduction in H_2Se and H_2Te .

The bond angles for the three compounds Cl_2O , Cl_2S , and Br_2Te mesh smoothly with this explanation. Since chlorine is much larger than hydrogen, we might expect greater repulsion in Cl_2O than in H_2O and, hence, a somewhat larger bond angle in Cl_2O . The same argument, however, would lead us to expect an F_2O bond angle between that for H_2O and Cl_2O . The observed 102° angle is not readily explained without some new argument.

NITROGEN

The nitrogen family has, in the valence orbitals, the electron configuration $ns^2np_x^1np_y^1np_z^1$. Three bonding orbitals are available, directed at right angles, and lead to an expectation of a 90° pyramidal arrangement without hybridization. Again, experiment is in comfortable agreement, the hydrides presenting the same trend shown by the oxygen family. The halogen compounds are also compatible except, again, for the small angle observed for NF_3 .

CARBON

Each element of the carbon family is found, experimentally, to form four equivalent bonds. The available orbitals can explain this *number* of bonds if we assume the electron configuration $ns^1np_x^1np_y^1np_z^1$. Without other evidence, however, the bonding orbitals suggest there might be three equivalent bonds formed at right angles, which use the p_x , p_y , and p_z orbitals, and a fourth, different bond formed at an undetermined angle by the spherically symmetrical s orbital. To eliminate this conflict with experiment, it is assumed that each of the four bonding orbitals is a mixture, or "hybrid," of the available bonding orbitals. Linear combinations of the available orbitals are considered ($as + bp_x + cp_y + dp_z$), and the coefficients a , b , c , and d are selected with two criteria in mind. Four sets of coefficients must be found (one set for each hybrid orbital), and

TABLE 17-3

Experimental Bond Angles for Some Compounds in the Oxygen and Nitrogen Families

H_2O	104.5°	F_2O	102°	Cl_2O	111°	—	—
H_2S	92°	—	—	Cl_2S	102°	—	—
H_2Se	91°	—	—	—	—	—	—
H_2Te	89.5°	—	—	—	—	Br_2Te	98°
NH_3	107°	NF_3	102°	—	—	—	—
PH_3	93°	—	—	PCl_3	100°	PBr_3	101.5°
AsH_3	91.5°	AsF_3	102°	$AsCl_3$	98°	$AsBr_3$	101°
SbH_3	91.3°	SbF_3	88°	$SbCl_3$	99.5°	$SbBr_3$	97°
—	—	—	—	$BiCl_3$	100°	$BiBr_3$	100°

these four sets must be selected so that they are *equivalent* and so that they are *mutually oriented at tetrahedral angles* ($109^\circ 28'$). You will recall that in discussing the orientation of a p_x orbital (which really occupies all space), we were guided by the angular properties. This orbital is considered to be oriented *along* the x -axis, because the probability of finding the electron is greater along this line than along any other line passing through the nucleus. In deciding how the hybrid orbitals will be oriented, we should follow the same reasoning—discover along what line the probability is a maximum. Our four bonds will be equivalent if the probability distribution along the four “bond-lines” are identical, and they will be properly oriented if the four “bond-lines” are directed through the vertices of a regular tetrahedron.

Upon this basis, we deduce the following set of hybrid orbitals:

$$\begin{aligned}(sp^3)_1 &= \frac{1}{2}(s + p_x + p_y + p_z) \\(sp^3)_2 &= \frac{1}{2}(s + p_x - p_y - p_z) \\(sp^3)_3 &= \frac{1}{2}(s - p_x + p_y - p_z) \\(sp^3)_4 &= \frac{1}{2}(s - p_x - p_y + p_z)\end{aligned}$$

Perhaps one of the most convincing aspects of the hybridization scheme is that these four sp^3 hybrid orbitals are not only equivalent and tetrahedrally oriented, but *they also represent the best possible combinations for concentrating the probability distribution along the “bond-lines.”* The concentration of probability along the “bond-line” is used by Pauling as a measure of bond strength, because a high directionality along a bond line implies a high overlap with the bonding orbital of an adjacent atom.

In summary, when the carbon family elements form four single bonds, they are tetrahedrally oriented, no matter what atoms are attached. This can be explained by considering that the bonding occurs through hybrid bonding orbitals, each of which is a linear combination of the available valence orbitals, s , p_x , p_y , and p_z . Confidence in the hybridization scheme derives from the observation that *the requirement of tetrahedral orientation produces maximum directionality* of the hybrid orbitals.

BORON

Each element of the boron family forms three equivalent bonds in the same plane and directed at the vertices of an equilateral triangle. Again, “mixing” of the available bonding orbitals is necessary to explain the number and orientation of the three bonds. The procedure for seeking suitable linear combinations of the s , p_x , and p_y orbitals follows the pattern given for carbon. Again the technique is successful. Suitable linear combinations are found, and the planar and equivalent sp^2 hybrid orbitals turn out to have maximum directionality.

BERYLLIUM

Each element of the beryllium family forms two equivalent bonds in a linear arrangement. The hybrid orbitals are simple in form and easy to visualize.

$$\begin{aligned}(sp)_1 &= \frac{1}{\sqrt{2}}(s + p_x) \\(sp)_2 &= \frac{1}{\sqrt{2}}(s - p_x)\end{aligned}$$

It is clear that these two hybrids are both directed along the x -axis. Since the s orbital is spherically symmetric, the p_x orbital determines completely the angular properties. The difference in algebraic sign of the p_x contribution in $(sp)_1$ and $(sp)_2$ causes the two hybrids to be oppositely directed. The equivalence of the two hybrids is indicated by the fact that each contains the same “admixture” of s orbital.

LITHIUM

The alkalis have but one bonding orbital and do not raise the question of bond angle.

HYBRIDS INVOLVING d ORBITALS

The same procedure is applicable to atoms whose valence orbitals involve d as well as s and p orbitals. Suitable linear combinations exist to explain the structures found in molecules involving transition elements (which use d orbitals in bonding). The geometries of some of these hybrid orbitals are shown in Table 17-4.

TABLE 17-4
Geometrical Properties of Some Hybrid Orbitals

Number of Bond Orbitals	Hybrid	Spatial Arrangement	An Example
2	sp	linear	BeF_2
	p^2	bent	H_2O
3	sp^2	trigonal, planar	BF_3
	p^3	trigonal, pyramidal	NH_3
4	sp^3	tetrahedral	CH_4
	dsp^2	tetragonal, planar	$\text{Ni}(\text{CN})_4^{2-}$
5	dsp^3	trigonal bipyramid	PCl_5
6	d^2sp^3	tetragonal bipyramid (octahedron)	$\text{Fe}(\text{CN})_6^{3-}$

The Electrostatic Model

The repulsions between pairs of valence electrons (whether used for bonding or not) provide an alternate basis for explaining the observed geometries in the simple molecules. In the electrostatic model, the tendency for electrons to stay as far apart as possible is taken to be the predominant factor in fixing bond angles. The principal advantage of this model is its simplicity, as shown again in a sweep across the Periodic Table (this time, from left to right).

LITHIUM

The alkalis involve but one electron pair in bonding, hence do not raise the question of bond angle.

BERYLLIUM

Each element in the beryllium family forms two bonds, hence involves two pairs of bonding electrons. These two pairs are separated as far as possible when the two bonds are oppositely directed along a line. Hence this model predicts a linear molecule, in agreement with experiment.

BORON

Each element in the boron family forms three bonds, hence involves three pairs of bonding electrons. These three pairs are separated from each other as far as possible when the three

bonds are in the same plane and directed at 120° angles to each other. The model is again in agreement with the observed structures of BF_3 , BCl_3 , etc.

CARBON

Each element in the carbon family forms four bonds, hence involves four pairs of bonding electrons. These four pairs are farthest separated in the tetrahedral orientation, in accord with the facts.

NITROGEN

Each element in the nitrogen family forms three bonds, but has another pair of electrons in a valence orbital. Here, too, each has four pairs of electrons, and a tetrahedral orientation of the four pairs is expected. The three bonds should be found along three of the four tetrahedral directions, forming a trigonal pyramid with $109^\circ 28'$ angles. This is in qualitative, but not quantitative, agreement with experiment, as shown in Table 17-3. Ammonia is quite close to the tetrahedral value, 107° , but PH_3 , AsH_3 , and SbH_3 are all near 92° . Perhaps the tetrahedral shape is not found because the electron pairs are nonequivalent. One pair is not used in bond formation. We can postulate that this extra pair exerts stronger repulsion on the bonding electrons than the bonding pairs exert on each

other. Unfortunately it is difficult to explain why this effect should be almost negligible for NH_3 but very large and about the same for PH_3 , AsH_3 , and SbH_3 .

OXYGEN

Of the four pairs of electrons in the bonding orbitals of oxygen, two pairs are shared in chemical bonds, and two pairs are unused in bonding. If these four pairs are tetrahedrally oriented, a bent molecule is expected. Turning again to the actual angles, we find they are all smaller than the tetrahedral angle of $109^\circ 28'$. The same effect that accounts for the closing of the NH_3 angle to 107° ought to be present, although to a greater degree, in water (in which there are two unused pairs of electrons pushing the HOH bond angle to a smaller size). This argument is in nice agreement with experiment, since water deviates from the tetrahedral bond angle by just about twice as much as does ammonia. The pleasure this observation brings is quite shattered, however, by observing the experimental angles of H_2S , H_2Se , and H_2Te . These angles are practically identical to the 92° bond angles observed in PH_3 , AsH_3 , and SbH_3 . If these large deviations from $109^\circ 28'$ are explained in terms of non-equivalent interactions between unused pairs and bonding pairs, then somehow the rationale for

the large deviations must be compatible with the almost constant bond angles near 90° .

FLUORINE

The halogens form but one bond and do not raise the question of bond angle.

Higher Numbers of Valence Electrons

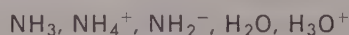
The idea that electron–electron repulsions are a factor in determining bond angles can be extended to the case of six electron pairs near an atom. The tetragonal bipyramid, or octahedral geometry, places the pairs far apart. If one of the pyramid apex positions is occupied by an unused electron pair, a tetragonal pyramid structure results among the bonds. If both of the pyramid apex positions are occupied by electron pairs, a square planar structure results.

In summary, both the hybridization and the electrostatic schemes furnish bases for qualitative explanation of observed bond angles. Each model presents some difficulty in dealing with the quantitative aspects, with the result that predictions made in the absence of experimental data have proven to be unreliable. At the introductory level, an empirical presentation is warranted. The deviations from the predictions require a much more sophisticated treatment.

Answers to Exercises and Problems

Exercise 17-1

Molecules that are isoelectronic often have similar molecular geometry. Comment on the bond angles you would expect in the molecules or ions listed. They are isoelectronic with CH_4 .



Answer

Methane, CH_4 , has 109° angles. Thus, from the generalization given, we could expect angles near that value. Those that have been measured are $109 \pm 10^\circ$.

Exercise 17-2

In Exercise 17-1 you suggested a bond angle in NH_3 and H_2O . Compare those with the experimental values of 107° and 105° respectively.

Answer

The experimental angles are near the tetrahedral angle expected, 109° .

Exercise 17-3

The compounds ClF and $\text{S}_4\text{N}_4\text{H}_4$ have been synthesized. What would you expect their molecular

structures to be? Predict what their melting temperatures might be relative to ice and to salt.

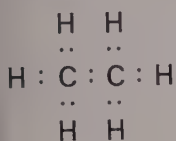
Answer

CIF should be a diatomic, molecular solid much like Cl_2 or F_2 . It should have a melting temperature lower than ice. The group NH is isoelectronic with S. Therefore a cyclic structure might occur. The known compound has alternating S and N atoms around the ring, but the student has no way to know that. The melting temperature should be above ice but below salt.

Exercise 17-4

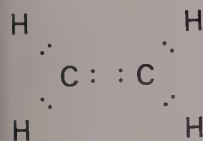
Convince yourself that each atom in the three molecules C_2H_6 (ethane), C_2H_4 (ethylene), and C_2H_2 (acetylene) has the electron configuration of a noble gas.

Answer



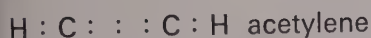
ethane

Each C has $8 e^-$, as Ne does in its valence orbitals. Each H has $2 e^-$, as He does.



ethylene

same



acetylene

same

Exercise 17-5

In Table 10-7, page 180, there are nine molecules isoelectronic with F_2 . Explain why these substances have low melting and boiling temperatures.

Answer

All the molecules isoelectronic with F_2 have the valence orbitals of each atom filled. The forces between molecules are the weak van der Waals type. Low temperatures supply sufficient energy to overcome these forces; so the substances melt and boil at low temperatures.

Exercise 17-6

When silica (SiO_2) is heated with carbon, the substance known as carborundum is formed. The empirical formula for carborundum is SiC. This material is important because it is almost as hard as

diamond but is much less expensive. What would you expect the structure of SiC to be? How can you account for its hardness?

Answer

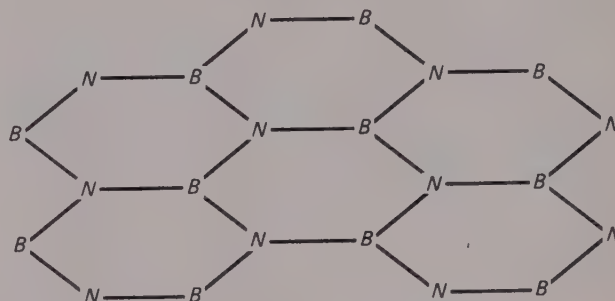
Probably SiC is a network solid. The hardness suggests this type since metals and molecular solids do not have high strengths.

Exercise 17-7

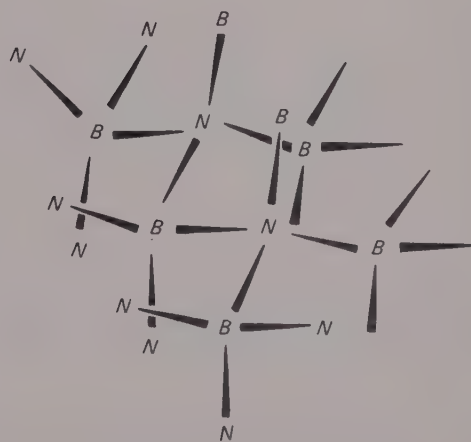
The compound boron nitride, BN, has been known for many years. It has a structure very similar to graphite. Recently, it has been possible to convert this material to the diamond structure, using very high temperatures and pressures. Draw one layer of the graphite-like structure and a portion of the diamond structure for boron nitride.

Answer

A graphitelike sheet of BN

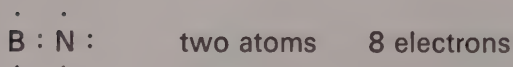
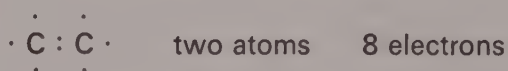


*A portion of diamondlike BN
(The student might use Textbook Figure 17-12 for a model.)*



Exercise 17-8

Show that boron nitride and carbon are isoelectronic. Compare the total electronic configuration for one boron atom plus one nitrogen atom with the total electronic configuration for two carbon atoms.

Answer**Exercise 17-9**

In Figure 16-8, page 321, the X-ray patterns for aluminum, copper, and sodium metal are shown. What type of crystal structure would you expect for copper?

Answer

The X-ray patterns of Al and Cu are the same in possessing alternation of two close-spaced, strong lines, separated by a single weak line. Both are cubic closest-packed crystals. Sodium is body-centered cubic.

Exercise 17-10

At room temperature, pure metallic iron has the same structure as sodium. When heated to about 1000°C, a phase transition occurs and iron assumes the face-centered cubic structure. This structure can be "frozen" in by very rapid cooling to room temperature. Compare the properties of the two forms of iron.

Answer

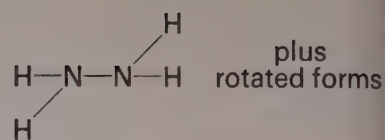
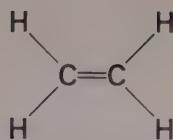
The body-centered form should be less dense than the "frozen" face-centered form. The former has an X-ray pattern like sodium, the latter one like aluminum.

Problem 1

Ethylene, C_2H_4 , has zero molecular dipole while hydrazine, N_2H_4 , has a large one. Explain. The atoms in each follow normal bonding rules.

Answer

The bonding arrangements are



In ethylene, the double bond maintains a planar structure and the four bond dipoles cancel. In hydrazine, there is pyramidal geometry around each nitrogen and rotation can occur around the N—N bond. Thus, a molecular dipole ($\mu = 1.9$ Debyes) results from the combination of the four bond dipoles.

Problem 2

Would you expect SiH_3F to have a molecular dipole? Explain your answer.

Answer

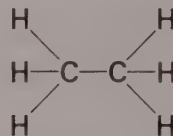
Yes. The combination of the three hydrogen-silicon bond dipoles would be in the opposite direction to the Si-F dipole, but they would not be equal in size.

Problem 3

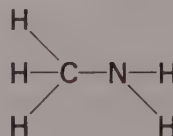
Consider the two compounds CH_3CH_3 (ethane) and CH_3NH_2 (methylamine). Why does CH_3NH_2 have an electric dipole while CH_3CH_3 does not?

Answer

The symmetry of ethane causes an exact cancellation of all bond dipoles:



In methylamine, however,



no such cancellation occurs, since C and N have different nuclear charge. Hence CH_3NH_2 is polar (measured μ is between 1.2 and 1.3 Debyes).

Problem 4

Consider the following series: CH_4 , CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4 . In which case will the molecules have electric dipoles? Support your answer by considering the bonding orbitals of carbon, the molecular shape of the molecules, and the resulting symmetry.

Answer

Since atoms with different ionization energies are bonded, one could expect the bonds to have some ionic character. But such bond dipoles result in a molecule with an electrical dipole only if the proper geometry exists. The tetrahedrally oriented bonds of carbon present a geometry in which dipoles will not cancel unless all four attached groups are alike. Such is the case only for CH_4 and CCl_4 . The other gaseous molecules have the following dipole moments:

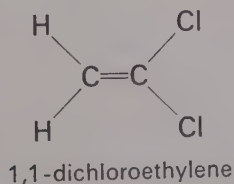
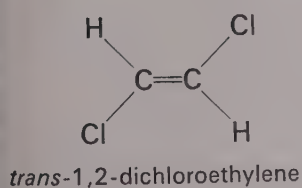
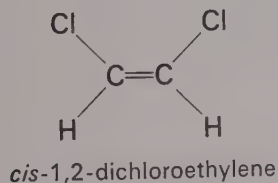
CH_3Cl	chloromethane	1.8 Debye
CH_2Cl_2	dichloromethane	1.6 Debye
CHCl_3	chloroform	1.0 Debye

Ball-and-stick models will be very useful here in showing that the electric dipoles of two C—Cl bonds do not cancel.

Problem 5

Draw the three isomers of dichloroethylene. Which will be polar molecules?

Answer



Chlorine has a greater tendency to acquire electrons than does either hydrogen or carbon. Consequently each carbon-chlorine bond can be

expected to have a bond dipole. The symmetries of 1,1-, and *cis*-1,2-dichloroethylene cause net addition of these dipoles to yield polar molecules. In the *trans* isomer there is an exact cancellation of the bond dipoles, by symmetry, giving a zero molecular dipole.

Problem 6

Would you expect liquid ammonia to be a good solvent for ionic compounds?

Answer

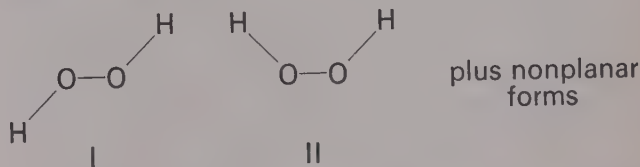
Yes. It has a dipole moment, as water does, so it could arrange itself around ions much as water does. The bonds formed provide the energy needed to break the bonds in the solute.

Problem 7

Hydrogen peroxide, H_2O_2 , has a moderate-sized molecular dipole. Describe the bonding orbitals used and propose a structure to explain the dipole. The atoms in H_2O_2 fit the normal bonding rules.

Answer

To fit the normal bonding rules, the atoms are connected so that oxygen forms two bonds and hydrogen one. The bonding orbitals are $1s$ for hydrogen and $2p$ for oxygen. The latter will lead to a bent molecule.

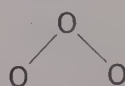


Structure I would have zero molecular dipole as the two bond dipoles cancel. Structure II or nonplanar forms would have a molecular dipole. The actual structure has an angle of about 94° between the two O—H bonds when viewed along the O—O bond.

Problem 8

Ozone, O_3 , has a molecular dipole. Suggest a structure.

Answer



The measured angle is 117° .

Problem 9

Considering comparable oxygen compounds, predict the shape of H_2S and H_2S_2 molecules. What bonding orbitals are used?

Answer

H_2S should be like H_2O . It has the same relative amount of hydrogen, and sulfur has the same number of valence electrons as oxygen. There should be p^2 bonding around the S atom, and a "bent" molecule should result:



Note: The HSH angle is somewhat smaller (92.2°) than that in H_2O (104.5°).

The H_2S_2 structure is like that of H_2O_2 . The HSS angle is 95° , again smaller than that in H_2O_2 .

Problem 10

Predict the type of bonding and the shape of the ion BF_4^- .

Answer

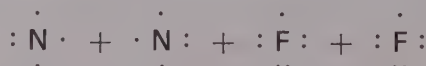
The boron atom has 3 valence electrons. These can be shared with three fluorine atoms. There is still a vacant valence orbital on the boron atom. A fluoride ion, itself having only filled orbitals, can form a bond by sharing one pair of electrons with that vacant boron orbital. The result is sp^3 bonding of the boron atom. Tetrahedral geometry is found as for CCl_4 .

Problem 11

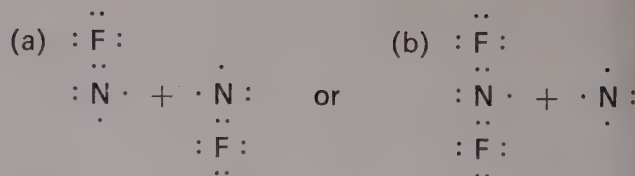
Predict the structure of the compound N_2F_2 from the electron dot representation of the atoms and the molecule.

Answer

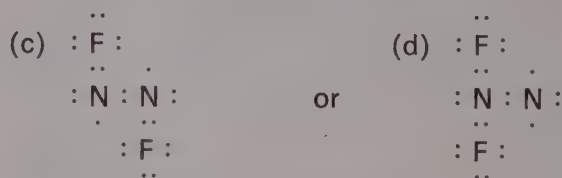
The structure might be approached in a succession of drawings. The atoms are:



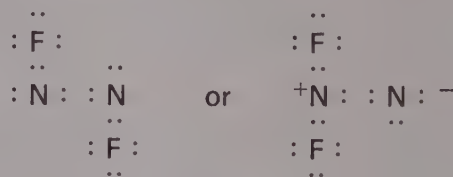
Each fluorine atom can form one bond, but there are two possible arrangements.



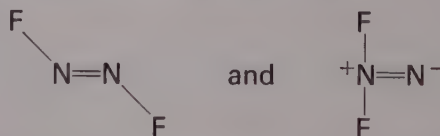
These groups can combine to give



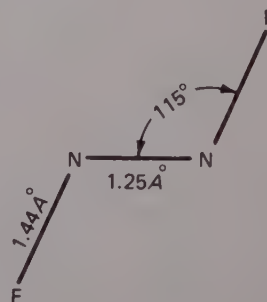
Arrangement (c) can satisfy its bonding capacity by forming a double bond. Structure (c) is favored relative to structure (d), which requires a charge separation:



These correspond to the structures



Both have been postulated, but at present the experiments favor (c), which has the following molecular dimensions.



Problem 12

Sulfur is made up of S_8 molecules; each molecule has a cyclic (crown) structure. Phosphorus contains P_4 molecules; each molecule has a tetrahedral structure. On the basis of molecular size and shape, which would you expect to have the higher melting point?

Answer

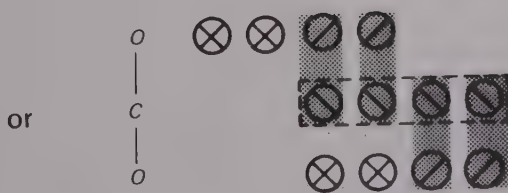
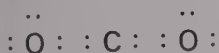
The building blocks are S_8 and P_4 . For these substances melting involves the overcoming of van der Waals forces between adjacent molecules; we must decide between which of these two types of molecules this force is greater. The magnitude of van der Waals forces varies directly with molecular size (perimeter) and depends upon molecular geometry. Both of these factors are more favorable for a strong interaction among sulfur molecules, hence the melting temperature of sulfur is expected to be higher. (Melting temperatures are: for sulfur, rhombic, 113°C ; monoclinic, 119°C ; for phosphorus, 44°C .) Notice that the masses of the particles are not a major factor.

Problem 13

The elements carbon and silicon form oxides with similar empirical formulas: CO_2 and SiO_2 . The former sublimates at -78.5°C and the latter melts at about 1700°C and boils at about 2200°C . From this large difference, propose the types of solids involved. Draw an electron dot or orbital representation of the bonding in CO_2 that is consistent with your answer.

Answer

The melting temperatures show that SiO_2 must be a network solid and that CO_2 must be a molecular solid.

**Problem 14**

Discuss the conduction of heat by copper (a metal) and by glass (a network solid) in terms of the valence orbital occupancy and electron mobility.

Answer

Copper is a better conductor than glass because the bonding electrons in copper are much more mobile than are those in glass. Metals are characterized as having few valence electrons, low ionization energies, and many valence orbitals available for occupancy. As a result of these factors, the bonding electrons are highly mobile, and they are not localized.

Network solids occur when all of the valence orbitals can become occupied through normal, covalent bonding in an interlinked, extensive structure. In covalent bonds, the electrons are rather localized in space, and lack the mobility necessary for conductivity.

Problem 15

Contrast the bonds between atoms in metals, in molecular solids, and in network solids in regard to:

- bond strength,
- orientation in space,
- number of orbitals available for bonding.

Answer

- Van der Waals bonds form between atoms or molecules without residual bonding capacity. They are characteristically quite weak—of the order of a few kcal/mole—as shown by low melting temperatures and low heats of vaporization. Metallic and covalent bonds are of the order of 30–150 kcal/mole, much stronger than van der Waals forces, as shown by high melting temperatures and high heats of vaporization.
- Bonds in van der Waals solids and metallic solids are not directional. This is shown in the softness of van der Waals solids and in the malleability of metals. Network solids have directional bonds linking the lattice, hence form hard crystals.
- Metallic solids are formed by atoms that have an abundance of empty or partially filled valence orbitals. Van der Waals solids are formed by atoms or molecules in which all valence orbitals are filled. Network solids

result when atoms form highly directed bonds. These bonds use all the bonding capacity of each atom.

Problem 16

How do you account for the following properties in terms of the structures of the solids?

- Graphite and diamond both contain only carbon. Both are high melting yet diamond is very hard while graphite is a soft, greasy solid.
- When sodium chloride crystals are shattered, plane surfaces are produced on the fragments.
- Silicon carbide (Carborundum) is a very high-melting, hard substance, used as an abrasive.

Answer

The Textbook shows the structures of graphite and diamond in Figures 17-12 and 13 and that of sodium chloride in Figure 17-24. Through class discussion, the silicon carbide structure can be predicted readily from the similar bonding capacities of silicon and carbon.

- The high melting temperatures of diamond and graphite are accounted for by the interlinked nature of the crystal structures. The diamond lattice has a three-dimensional, interlinked structure. The graphite lattice has two-dimensional, interlinked planes, successive planes being held together weakly. The two-dimensional, infinite network is sufficient to give a high melting temperature (as is true for the micas, shown in Textbook Figure 17-15, p. 341). The hardness of diamond is related to the fact that any cleavage plane in diamond is crossed by many bonds. Graphite, with its two-dimensional structure, has planes that exert only weak forces toward other such planes or other substances. These weak forces give graphite its softness and the property that makes it act as a lubricant in some circumstances.
- Sodium chloride is an ionic solid whose crystal is made up of a lattice of evenly spaced sodium ions surrounded by regularly spaced chloride ions. The plane surfaces produced on cleavage are related to this regularity. Cleavage occurs most readily

between neutral planes (same number of sodium and chlorine atoms).

- Crystals of SiC consist of silicon and carbon atoms bound together by strong chemical bonds that form a three-dimensional network solid having the usual accompanying properties—hardness and high melting temperature.

Problem 17

If you were given a sample of a white solid, describe some simple tests you would perform to help you classify the solid as molecular, network, ionic, or metallic.

Answer

It is difficult to decide the nature of the bonding in a solid through simple measurements. Nevertheless, certain significant correlations provide valuable clues. Finally, *the answer must be based upon a general pattern of self-consistency among several properties, since none is decisive.*

- Behavior on warming.* In general, ionic solids and network solids tend to have high melting temperatures, whereas molecular solids (van der Waals solids) tend to have low melting temperatures. Hence an initial sorting of molecular solids can be based upon what happens when the solid is heated to a few hundred degrees Celsius.
- Solubility in water and electrolyte behavior.* The solubility in water provides a further basis for classification. Though it is by no means true that all ionic solids have high solubility in water, many of them have detectable solubility. Furthermore, the substances that are commonly known to form ionic solids form conducting solutions. Hence the combination of solubility in water and ionic conductivity of the resulting solution provides a reasonable basis for assuming an ionic solid. Much reservation is attached to this statement, however, since many molecular substances have measurable solubility in water, and some of these form conducting solutions (e.g., HCl, H_3PO_4 , acetic acid, benzoic acid, ammonia).

- (c) *Hardness.* Ionic solids and network solids are often hard; molecular solids tend to be soft.
- (d) *Conductivity of melt.* Well-recognized ionic solids conduct electricity when melted. Hence electrical conductivity in the pure liquid suggests that it will form an ionic solid.

Problem 18

If elements A, D, E, and J have atomic numbers 6, 9, 10, and 11 (in order), write the formula for a substance you would expect to form between the following:

- (a) D and J; (d) E and E;
 (b) A and D; (e) J and J.
 (c) D and D;

In each case describe the forces involved between the building blocks in the solid state.

Answer

First note that:

A has atomic no. 6 and 4 valence electrons;
 D has atomic no. 9 and 7 valence electrons;
 E has atomic no. 10 and 0 valence electrons;
 J has atomic no. 11 and 1 valence electron.

- (a) D and J would form a compound, JD, which would involve ionic bonding and have an ionic crystal lattice.
- (b) A and D would probably form a compound, AD₄, a covalently bonded, nonpolar compound. Atoms that have half-filled valence orbitals tend to form covalently bonded compounds with other atoms. The solid would likely be molecular, van der Waals forces holding adjacent molecules together.
- (c) D and D would tend to form a molecule having formula D₂. Since this molecule would have no unused bonding capacity, it would likely form a molecular solid, held together by the very weak van der Waals forces.
- (d) E and E would not combine, since these atoms have no orbitals available for bonding. This same situation is found in the noble gases. The elements Ne, Ar, Kr, and Xe crystallize with the cubic close packed structure. Helium forms a solid only under pressure (25 atm minimum). The structure is probably hexagonal close packed. Radon

has not been studied in the solid state.

- (e) J and J would form a metallic solid because there is but one valence electron per atom and four available valence orbitals.

Problem 19

Predict the order of increasing melting temperature of these substances containing chlorine: HCl, Cl₂, NaCl, CCl₄. Explain the basis of your prediction.

Answer

Melting involves the overcoming of forces between the units of which the solid is made. Three of the given substances, HCl, Cl₂, and CCl₄, would be expected to form molecular solids (no unused bonding capacity, and similar ionization energies); the other, NaCl, would be expected to form an ionic solid (great difference in ionization energies). The coulombic forces holding an ionic solid together are strong, hence NaCl would be expected to have a high melting temperature.

The van der Waals forces holding the molecular solids together are weak. Of the three, CCl₄, owing to its large and complex surface, should have the highest melting temperature. The size of the Cl₂ molecule should be greater than that of HCl and, on this basis, its melting temperature should be higher. The possibility of hydrogen bond formation among HCl molecules works the other way, making a positive prediction difficult. The observed melting temperatures are: HCl, -114°C; Cl₂, -101°C; CCl₄, -22.8°C; NaCl, 801°C.

Problem 20

Identify all the types of bonds you would expect to find in each of the following crystals:

- | | |
|---------------------|-----------------------|
| (a) argon | (f) Al |
| (b) water | (g) CaCl ₂ |
| (c) methane | (h) KClO ₃ |
| (d) carbon monoxide | (i) NaCl |
| (e) Si | (j) HCN |

Answer

v = van der Waals
 c = covalent
 i = ionic

h = hydrogen bonding
 m = metallic

- (a) v
- (b) c within molecule; v, h between molecules
- (c) c within molecule; v between molecules
- (d) c within molecule; v between molecules
- (e) c
- (f) m
- (g) i
- (h) i, c within ClO_3^- ion
- (i) i
- (j) c within molecule; v, h between molecules

Problem 21

Aluminum, silicon, and sulfur are close together in the same row of the Periodic Table, yet their electrical conductivities are widely different. Aluminum is a metal; silicon has much lower conductivity and is called a semiconductor; sulfur has such low conductivity it is called an insulator. Explain these differences in terms of valence orbital occupancy.

Answer

This comparison shows the importance of orbital occupancy in fixing conduction properties. The orbital occupancies are:

	1s	2s	2p	3s	3p
Al					
Si					
S					

Aluminum is the only one of these elements that has more valence orbitals than valence electrons, hence it is the only metal of the three.

Silicon, which has four valence orbitals and four valence electrons, can form a three-dimensional network, with the result that every atom can obtain a noble gas arrangement by sharing pairs of electrons with adjacent atoms. Under these bonding circumstances the conductivity is low. Sulfur, which has six valence electrons and four valence orbitals, can fill its orbitals by forming a molecule. Hence the interactions that hold the sulfur crystal together are the weak van der Waals forces. Under these bonding circumstances, the conductivity is almost negligible, hence a substance like sulfur can be used as an insulator.

Problem 22

Consider each of the following in the solid state: sodium, germanium, methane, neon, potassium chloride, water. Which would be an example of

- (a) a solid held together by van der Waals forces that melts far below room temperature;
- (b) a solid with a high degree of electrical conductivity that melts near 100°C ;
- (c) a high melting, network solid involving covalently bonded atoms;
- (d) a nonconducting solid which becomes a good conductor upon melting;
- (e) a substance in which hydrogen bonding is pronounced?

Answer

- (a) neon, methane;
- (b) sodium;
- (c) germanium;
- (d) KCl;
- (e) H_2O .

Problem 23

Each of three bottles on the chemical shelf contains a colorless liquid. The labels have fallen off the bottles. They read as follows.

Label No. 1	Label No. 2	Label No. 3
<i>n</i> -butanol $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ molar mass = 74.12 g	<i>n</i> -pentane $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ molar mass = 72.15 g	diethyl ether $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ molar mass = 74.12 g

The three bottles are marked *A*, *B*, and *C*, and a series of measurements were made on the three liquids to permit identification. The following data were obtained.

	m.t.	b.t.	density	$\Delta H_{\text{vap}}'$	solubility in water
Liquid <i>A</i>	-131.5°C	36.2°C	0.63 g/cc	85 cal/g	0.036 g/100 ml
Liquid <i>B</i>	-116	34.6	0.71	89.3	7.5
Liquid <i>C</i>	-89.2	117.7	0.81	141	7.9

Which liquid should be given Label No. 1, Label No. 2, Label No. 3? Explain how each type of measurement influenced your choices.

Answer

Label 1 is correct for liquid *C*, Label 2 for *A*, and Label 3 for *B*.

Little chance for initial discrimination is offered by the melting temperatures. They do not differ sufficiently. Since the boiling temperature of substance *C* is so much higher than the other two, there is some chance for discrimination. The three different molecules exhibit essentially covalent bonding, and hence probably form molecular solids. Only *n*-butanol can form hydrogen bonds. These bonds would make it difficult to separate the molecules from each other and would explain the high boiling temperature and $\Delta H_{\text{vap}}'$ of *C*. Hydrogen bond formation is also consistent, liquid *C* having the highest density (tightest packing) and the highest solubility in water. Liquid *C* is No. 1.

The density varies so little that it is best used to confirm, not predict.

The $\Delta H_{\text{vap}}'$ is also best used for confirming predictions, not making them.

The knowledge that the solubility of *A* is so much lower than the others is a useful bit of data. The *n*-pentane has none of the characteristics commonly possessed by water-soluble molecules. It is nonpolar, can form no hydrogen bonds, and is not ionic. These factors are also consistent with these facts: it has the lowest melting temperature, boiling temperature, $\Delta H_{\text{vap}}'$, and density, due to the very small forces that exist between adjacent molecules. Liquid *A* is probably No. 2.

This leaves *B* for No. 3. Diethyl ether is a bent molecule (p^2 bonding on the oxygen) which is polar. This would explain some weak attractions between molecules, hence the low melting temperature. The low boiling temperature and $\Delta H_{\text{vap}}'$ could be explained by assuming that the kinetic energy at these temperatures is sufficient to break the weak attractions caused by polar molecules. The high solubility in water is consistent with the fact that water molecules may be hydrogen bonded to the oxygen, and also with the expected polar nature of the molecule.

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

Nitrogen is a gas at temperatures above 77°K (−196°C). Very little energy is required to change nitrogen from solid to liquid to gas. Nevertheless, kinetic energies corresponding to thousands of degrees Kelvin cannot cause appreciable decomposition of the N₂ molecules.

1. What are the forces acting to hold the nitrogen molecules, N₂, together in the liquid phase? Describe briefly the nature of these forces.

Answer

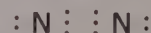
Van der Waals forces. Van der Waals forces

are electrical forces due to the interaction between electrons of one atom and the nucleus of a second atom, but from a relatively long distance, because the valence orbitals are all filled.

2. What is the nature of the chemical bond between the two nitrogen atoms in the N₂ molecule?

Answer

The chemical bond in an N₂ molecule is composed of three pairs of electrons shared between the two nitrogen atoms.



This produces a very strong covalent bond.

Questions 3–8 use information given below.

Substance	Melting Temperature (°K)	Boiling Temperature (°K)
(1) Helium	3.3	4.1
(2) Sodium chloride	1073.4	1686
(3) Carbon tetrachloride	250	349.8
(4) Carbon dioxide	—	sublimes at 194.5
(5) Silicon dioxide	about 2000	about 2500
(6) Diamond	above 3800	about 4500
(7) Methane	89	111
(8) Water	273	373

3. In which of the substances, if any, is the intermolecular force of attraction mainly due to van der Waals forces?

Answer: 1, 3, 4, 7.

4. Which of the above substances, if any, forms a molecular solid made up of polar molecules?

Answer: 8.

5. In which of the substances, if any, does hydrogen bonding occur?

Answer: 8.

6. According to the data given, in which of the solid substances do the weakest bonds exist?

Answer: 1.

SUGGESTED QUIZ QUESTIONS

7. Which of the solid substances, if any, forms bonds that are predominantly ionic?

Answer: 2.

8. Explain the differences in melting temperatures and boiling temperatures between carbon dioxide and silicon dioxide in terms of the types of bonding involved.

Answer

The low sublimation temperature for carbon dioxide indicates the presence of weak intermolecular van der Waals forces and small molecules. Carbon in CO_2 satisfies its bonding capability by forming two double bonds to two oxygen atoms. These CO_2 molecules are then held together by weak van der Waals interactions. On the other hand, the extremely high melting temperature and boiling temperature for silicon dioxide indicate the presence of strong bonds. This occurs because silicon forms four single bonds to four oxygen atoms, giving a network solid.

9. By way of generalization, as the number of electrons in a molecule increases the van der Waals forces between molecules (increase or decrease).

Answer: Increase.

10. How does adding traces of other elements to metals, such as adding carbon to iron, often make the resulting alloy harder and more brittle? Explain in terms of bonding.

Answer

Metallic bonds form when there are several empty bonding orbitals available to the valence electrons. This permits the valence electrons freedom of movement between the positive ions in the metal. The addition of an element having the property of forming more directed bonds (having valence orbitals more completely filled) utilizes some of the freely moving electrons in forming more directed covalent-type bonds. These directed

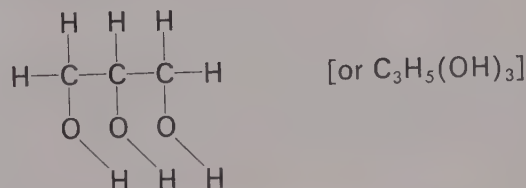
bonds give, locally, the character of a network solid, contributing to hardness and brittleness.

11. Explain why aluminum is a good conductor of heat and electricity whereas pure silicon is not.

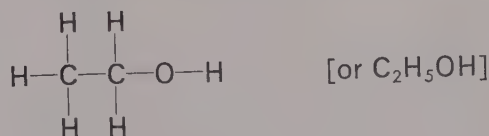
Answer

Aluminum has three valence electrons and four valence orbitals. Although the metallic bonding that occurs in aluminum is more directed than it is in some of the other metals which have even more available empty bonding orbitals, the electrons are still relatively free to move about between the positive aluminum ions. Silicon, however, has four valence electrons (as does carbon) and has four valence orbitals. This makes an ideal situation for the formation of four directed covalent bonds that utilize all the available electrons and valence orbitals. Having no free electrons, silicon is a poor conductor of electricity and heat.

12. Glycerin,



is far more viscous than ethyl alcohol,

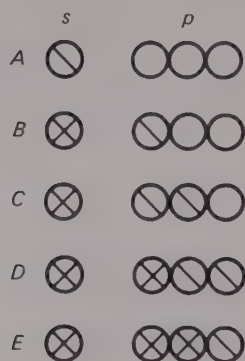


Why?

Answer

Glycerin, having three times as many OH groups per molecule, can form many more hydrogen bonds per molecule. This increases the net attraction between all the molecules, and hence increases resistance to flow.

To answer Questions 13–18, consider the following orbital representations:



Note: Some of these same questions (15–18) were included in the quiz suggested for Chapter 10.

13. Which of the elements given, if any, could be expected to form metallic bonds?

Answer: *A* and *B* (unless *B* is boron).

14. Which, if any, could be expected to form a network solid?

Answer: *C* (and *B* if it is boron).

15. Which, if any, should form a covalent bond with like atoms in the solid state?

Answer: *C*, *D*, and *E*.

16. What combinations of two elements from the list would form ionic solids?

Answer

AE, *A₂D*, and possibly *A₂D₂* peroxides.

17. Write the empirical formula for a compound formed by the combination of *C* and *D*.

Answer: *CD₂*.

18. Write the empirical formula for a compound formed by combining *D* and *E*.

Answer: *DE₂*.

The Chemistry of Carbon Compounds



Intent and Approach

It should be made very clear that the chemical principles that govern the behavior of organic compounds are in no way unique; that we are not dealing with a new "kind" of chemistry. The classification of organic chemistry as a definite area of study is primarily one of convenience, because the number of carbon compounds is enormous and because their typical behavior is not what is ordinarily found for inorganic compounds, whose chemistry deals more with ionic substances than with nonionized, covalent molecules. Part of this philosophy is to show the applicability of the chemical principles already studied. This thread runs through the remaining four chapters.

Coupled with the central idea of the importance of structure and the related concept of isomerism is the great versatility of carbon in using its four valence orbitals to form compounds. The three-dimensional possibilities of

bond formation to a tetravalent atom can give rise to great structural complexity.

The purely descriptive aspects of organic chemistry (the uses of esters as flavors and perfumes, the structures of common polymers, the structures of complex compounds such as drugs, dyes, etc.) should be minimized. Biochemistry is introduced briefly.

The aims of this chapter on the chemistry of carbon compounds are chiefly three: (1) to show the importance of structural arrangement of the atoms of which compounds are composed; (2) to introduce the chemistry of bond-breaking and bond-making in compounds in which the bonds are essentially covalent in nature; and (3) to show how large numbers of individual compounds can be grouped into classes according to the similarities in their behavior caused by functional groups.

Outline

The sources of organic compounds are the first topic (18-1).

Hydrocarbons, both saturated and with multiple bonds, are described (18-2).

Oxidation, from hydrocarbons to alcohols, ketones, aldehydes, and acids, follows (18-3).

Amines (18-4) and formation of esters and amides (18-5) illustrate some organic reactions.

Benzene (18-6) and other aromatic compounds (18-7) show more complex molecules.

Addition and condensation polymers (18-8) are used to introduce this important field. The section on nylon (18-9) brings detail to a well-known polymer.

Section 18-10, sugars, leads from organic to biochemistry. Disaccharides are mentioned (18-11).

Biological polymers (18-12) include the major structural materials of plants and animals—cellulose and protein.

Enzymes illustrate the connection between what the student has been learning and chemistry in living organisms (18-13).

Section 18-14 reveals a part of the energy production by an organism.

New Concepts

1. The use of *functional* groups to describe a general type of behavior.
2. The substitution (or replacement) reaction. Formation of a new bond as an old one is broken.
3. The chemistry in the body is fundamentally no different from that in a test tube.
4. Specific arrangements in polymers have an effect on their properties.
5. Cyclic systems of reactions are prominent in living systems.

SCHEDULE AND RELATED MATERIAL

Suggested Time : 10 days

Text Section	Topic and Other Work	Exercises	Problems		
			Easy	Medium	Hard
18-1	Sources of Carbon Compounds				
18-2	Hydrocarbons and Their Reactions	1-3	1, 2		3
18-3	Oxidation of Organic Compounds <i>Film:</i> Synthesis of an Organic Compound	4, 5	4, 9	5, 6	7, 8
18-4	Amines (Organic Bases)		10	11	
18-5	Acid Reactions <i>Film:</i> Mechanism of an Organic Reaction	6	12-15		16, 17
18-6	Benzene			18	
18-7	Benzene and Aromatic Compounds				19
18-8	Polymers Expt. 39, Some Reactions of Hydrocarbons and Alcohols			20	
18-9	Nylon, a Polymeric Amide			21-23	24
18-10	Sugars, Simple Biological Compounds	7-9			
18-11	Disaccharides				
18-12	Some Biological Polymers: Starch, Cellulose, and Protein <i>Film:</i> Biochemistry and Molecular Structure	10		25	
18-13	Enzymes				
18-14	Energy Sources in Nature				

Expt. 40, The Preparation of Esters, can be done anytime after Expt. 39.

Development

18-1 Sources of Carbon Compounds

This section serves to set the stage for the diversity of carbon-containing substances. It does not discuss the various ways these compounds are obtained from coal or oil. It does, however, give some reasons for the large number of carbon compounds. The *Background Discussion*, page 386, takes up the opposite problem "Why do other elements *not* form more compounds?"

18-2 Hydrocarbons and Their Reactions

This class of compounds is of minor importance because saturated hydrocarbons take part, in one sense, in relatively few reactions. On the other hand, since petroleum is a complex mixture of saturated hydrocarbons, they are quite important as the starting point for a variety of materials. The *Background Discussion* tells how some of these materials are made.

Unsaturated carbon compounds contain the multiple carbon-carbon bonds described in Chapter 10 (p. 182). Use this opportunity to show the applicability of previously studied principles to carbon chemistry. The compounds with double bonds are called alkenes, and the names end in -ene. Compounds with triple bonds are alkynes (acetylene is a nonsystematic name).

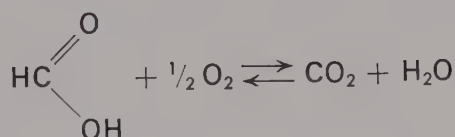
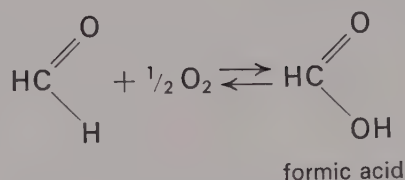
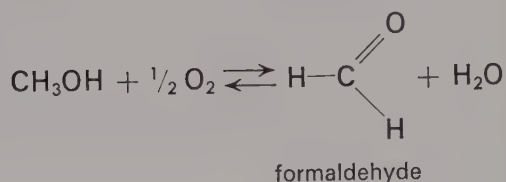
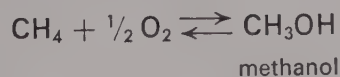
The reason for functional groups and the use of —R for nonreactive moieties are introduced. Stress the first as a great simplification based on the observation that similar compounds, e.g., alcohols, behave in a similar way.

If you wish to introduce organic nomenclature, this is the section to begin. It is not recommended for the usual one-year course.

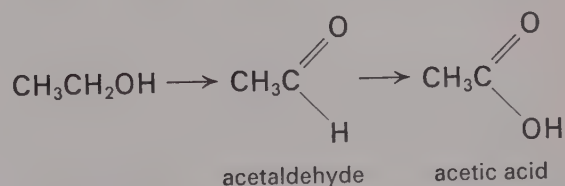
18-3 Oxidation of Organic Compounds

The most highly oxidized condition of a single carbon atom is CO_2 . The most reduced condition of a single carbon atom is methane, CH_4 . Between these extremes lie three other levels of oxidation, and the whole series of reactions can

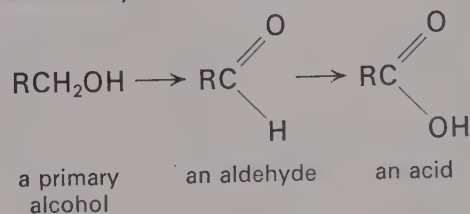
be carried out to give the compounds shown in the following equations:



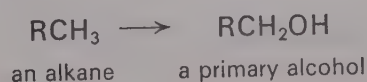
Oxidation of Higher Homologues. Ethanol can be oxidized to an aldehyde and this, in turn, to an acid in exactly the same way as methanol:



Homologous primary alcohols can be oxidized in the same way:

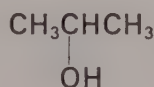


The first step in these series, starting from the alkane, can be written

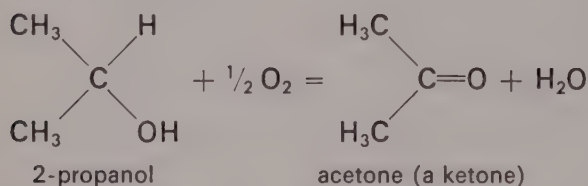


but this process cannot be carried out to give good yields of a single product; mixtures of oxidation products are formed. The oxidation of methane to methanol, on the other hand, is actually a feasible process.

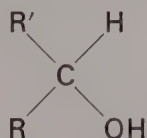
Oxidations of Other Kinds. One of the advantages of writing equations in a partial form, shown earlier for formaldehyde, is that it permits us to make reasonable predictions about the way in which related compounds will behave. For example, what would we predict to be the immediate (i.e., two-electron change) oxidation product of 2-propanol,



We would write

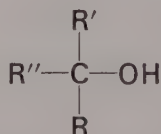


Secondary alcohols, of which 2-propanol is an example, have the generalized structure



where R and R' are alkyl groups (methyl, ethyl, propyl, etc.). These alcohols oxidize to *ketones*.

It may be pointed out to the students that there is a third class of alcohols—tertiary alcohols—in which the C—OH grouping carries three alkyl groups:



They can be oxidized only by very strong reagents, in which case smaller fragments (containing fewer carbon atoms) are formed. This is a subject that cannot be profitably discussed in the time available and should be explored further

only by those students who wish to consult textbooks of organic chemistry.

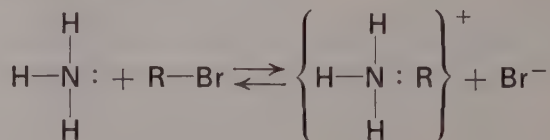
Film, SYNTHESIS OF AN ORGANIC COMPOUND,

fits here. See p. 384 for summary.

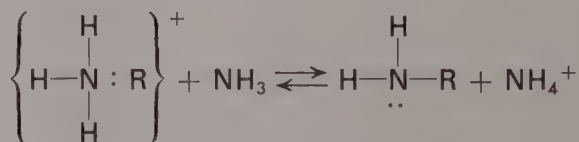
18-4 Amines (Organic Bases)

Amines are the typical organic bases. As bases they have about the same strength as ammonia. (*Note:* It would be reasonable to expect that, in RNH_2 , the strength of the amine as a base—that is, its dissociation constant—would vary as the nature of R varied. This is true, but a detailed discussion of the relationship between base strength and the structure of the group R would be too involved for this course.)

The formation of an amine by the reaction of ammonia with an alkyl halide (using here an alkyl bromide as the example) proceeds according to:

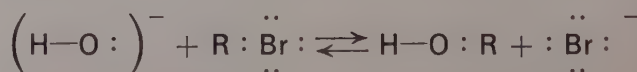


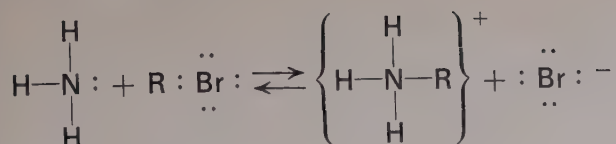
In the presence of a large excess of ammonia, simple proton exchange between RNH_3^+ and NH_3 in the acid-base equilibrium



will result in the formation of the free amine, RNH_2 .

Special attention should be paid to the resemblance between ammonia plus an alkyl halide and the reaction of an alkyl halide with hydroxide ion:





18-5 Acid Reactions

Esters and amides are discussed. These two types of functional groups are introduced to allow discussion of some important classes of polymers.

Film, MECHANISM OF AN ORGANIC REACTION,

fits here. See p. 385 for summary.

18-6 Benzene

An important thing to fix in the student's mind is *what the structure of benzene represents*. We do not have a satisfactory representation, but we do know the properties. Analysis and molar mass tell us that benzene is C_6H_6 . X-ray and electron diffraction tell us that the six carbons are in a flat ring, with a regular, hexagonal shape. All the carbon-carbon bonds are the same length, and all the C-H bonds are the same.

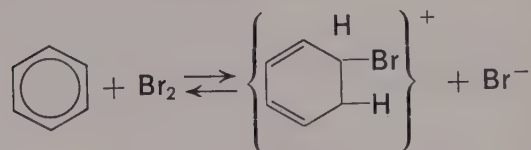
The symbol used, , is a modern one

based on the molecular orbital theory of benzene. It is now widely accepted for simple aromatic molecules and used in much of the literature. If you expanded the discussion of Section 10-5 to cover overlap of π orbitals, this symbol will give no trouble. Otherwise, just present it as a way of representing the facts as listed in Section 18-6.

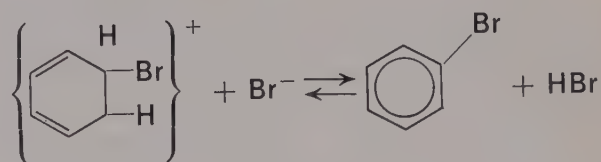
18-7 Benzene and Aromatic Compounds

The "aromatic" arrangement, with the properties listed in the previous section, has its own chemistry—somewhat between that of saturated and unsaturated hydrocarbons. The substitution reaction with Br_2 is a good example. Ethylene adds Br_2 to give 1,2-dibromoethylene. Ethane

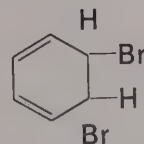
does not react. Benzene "substitutes" one Br atom for one H atom to give bromobenzene. The reaction is believed to go through the following steps. First an intermediate forms



which then loses the proton (on the same carbon as Br) to give

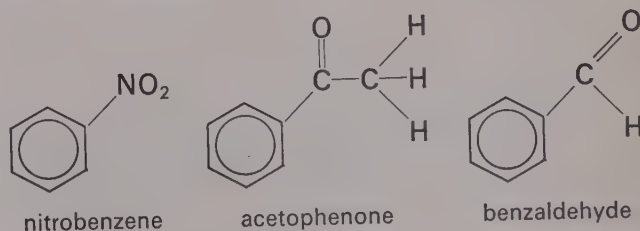


The great stability of the benzene ring, with its six electrons uniformly disposed over the ring, accounts for this result. The recovery of the aromatic structure shown in the last equation is quite exothermic; bromobenzene is much more stable than the other possible final product formed by adding the second bromine.



1,2-dibromo-3,5-cyclohexadiene

The aromatic substitution reaction produces an enormous number of benzene derivatives such as the following



By altering the introduced groups, a host of compounds can be made. These reactions, however, are beyond the scope of discussion you will have time for.

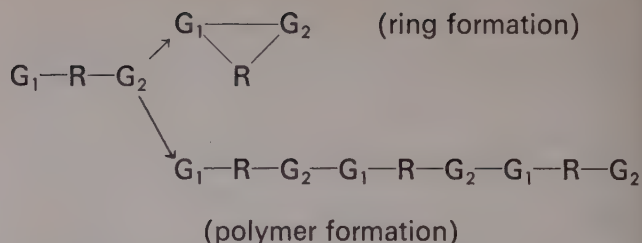
**Expt. 39, SOME REACTIONS OF
HYDROCARBONS AND OF
ALCOHOLS**

fits here. See p. 227 in the Laboratory Guide.

18-8 Polymers

18-9 Nylon, a Polymeric Amide

These sections deal with several kinds of polymers. The important thing is to clarify the polymerization process. One kind of molecule which can take part in polymerization is that which has two points (or groups) within one molecule which can react with each other. Let us designate the two functional groups, G_1 and G_2 , and the starting compound (monomer) as G_1-R-G_2 . Then we have two possibilities:



Although of interest, ring formation does not lead to polymers, hence will not be discussed.

You can use the following simple way to explain polymerization. See Figure 18-1. Have available eight or ten spring-type clothespins, all alike. Describe one as a molecule with two functional groups (the jaws, and one of the thin tail pieces). It is a monomer. Show "dimer formulation," and compare the structure with that of the monomer. The dimer still has the same two groups available for reaction. Then continue the "chain" as shown below. Finally,

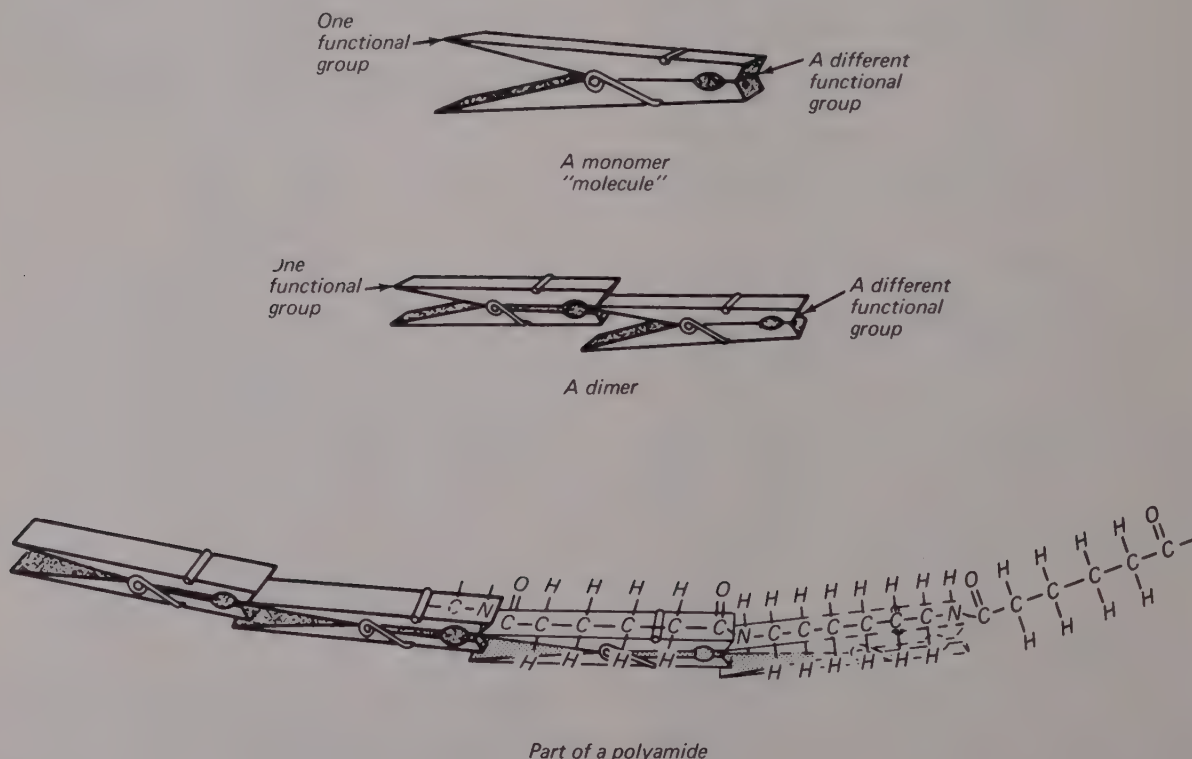


FIGURE 18-1

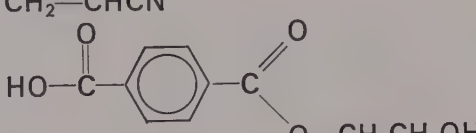
A simple representation of polymerization.

DEVELOPMENT

relate this model to a specific reaction, and write the formulas on the board.

Next point out that the different classes of polymers arise when the functional groups are varied, giving polyamides, polyethylene, etc. Vari-

ations within the class come from changes in the other (nonfunctional) part of the monomer. Some general idea of the composition of many common polymers can be gained from the following table.

Trade Names	Monomer	Formula	Melting temp., °C
polyethylene	ethylene	$\text{CH}_2=\text{CH}_2$	110
Saran	vinyl chloride	$\text{CH}_2=\text{CHCl}$	variable
	vinylidene chloride	$\text{CH}_2=\text{CCl}_2$	—
Teflon	tetrafluoroethylene	$\text{CF}_2=\text{CF}_2$	350
Viton	hexafluoropropylene	$\text{CH}_2=\text{CFCF}_3$	—
Neoprene	chloroprene	$\text{CH}_2=\text{C}(\text{Cl})\text{CH}=\text{CH}_2$	—
natural rubber	isoprene	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$	28
Styrofoam	styrene	$\text{CH}_2=\text{HC}-\text{C}_6\text{H}_5$	~ 200
Orlon	acrylonitrile	$\text{CH}_2=\text{CHCN}$	> 200
Dacron, Mylar	—		260

Other sources of information are:

J. K. Stille, *Introduction to Polymer Chemistry*, Wiley, N. Y., 1962.

F. Bueche, *Physical Properties of Polymers*, Interscience, N. Y., 1962.

18-10 Sugars, Simple Biological Compounds

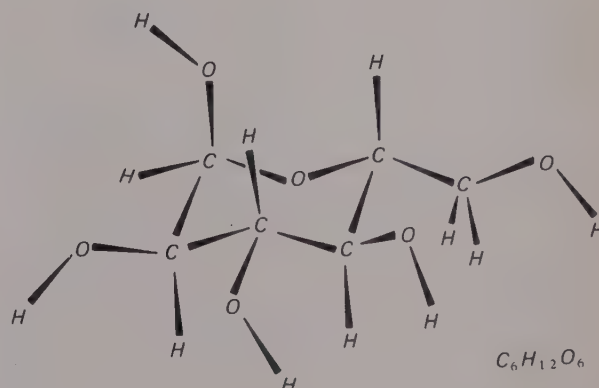
18-11 Disaccharides

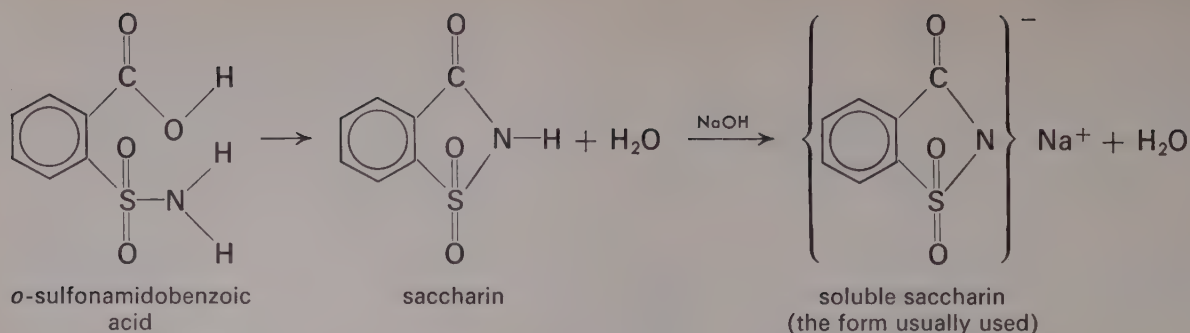
You will notice that the structural formula given in the Textbook for the glucose chain does not show the asymmetric carbon feature. That feature makes up a whole field of chemistry and is not, at this point, needed by a beginner. A careful observer may see in the ring form the placement of some OH groups above the ring, and others, below the ring. Such a student can be told that different isomers result from the different arrangements. He is not likely to benefit much from a discussion of polarized light, since he probably hasn't studied ordinary light much yet.

The ring structure does not give all details. Glucose actually has a "chair" configuration

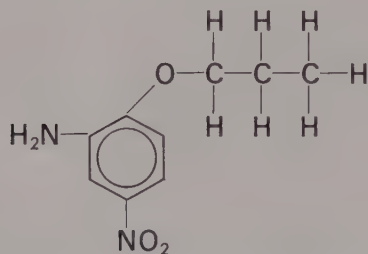
(below), not the planar configuration used throughout this chapter. Again, the use of the more complicated formula is unwarranted.

The word *saccharide* may seem strange, but most pupils know saccharin and its use as a sugar substitute. The word origin is the Sanskrit term *sakhara* for sugar which was first used extensively in India. Saccharin is a good compound to use to show that sweetness is not unique to the sugar structure.





Note that saccharin is an "inner" amide—that is, an amine group combined with an acid group of the same molecule. This material is about 500 times as sweet as sucrose. Another, even sweeter, substance (4000 times sucrose) is *n*-propoxy-2-amino-4-nitrobenzene:



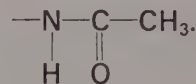
18-12 Some Biological Polymers: Starch, Cellulose, and Protein

These substances are given mainly as examples of polysaccharides and to set up their use in showing the importance of structure. It is best not to go deeply into their chemistry (for instance, the production of rayon is too complicated).

The soluble portion of natural starch is called amylose (molar mass = 10,000–50,000 g) and makes up 10–20% of the material. The slightly soluble portion is amylopectin. It is much larger than the soluble part (molar mass $\approx$ 50,000–100,000). Branching is detected by reactions that occur only at glucose units that terminate a chain. One "end" is found for each 25–30 glucose units. Since amylopectin consists of about 500 of these units, branching must exist. The amylose polymer is shown on Textbook page 374. Amylopectin is made of the same monomer, but branching occurs from some of the carbons that are not part of the ring.

The cellulose polymer is also shown on page 374 of the Textbook. Current evidence suggests that this is a completely linear polymer (molar mass = 300,000–500,000 g). Cellulose occurs in wood, cotton, flax, hemp, and jute. The determination of the molar mass of a polymer is very difficult. Consequently, published values are frequently given as a range rather than a specific number. Large molar mass and moderate solubility render freezing temperature determinations of little value. For example, one gram of polymer having a molar mass of 100,000 when dissolved in 100 grams of benzene would lower the freezing temperature only $5 \times 10^{-4} \text{C}^\circ$. Measurement of osmotic pressure is much more useful. The presence of a solute makes the vapor pressure of a solution lower than that of the solvent. If solution and solvent are separated by a membrane which is not permeable to the solute, then at equilibrium a hydrostatic head will exist on the solution side.

The hard shell on crustaceans (shrimp, lobster) and insects (beetles) is made of a polysaccharide called chitin (hardened with CaCO_3). Chitin has a structure like starch and cellulose except that in each glucose one $-\text{OH}$ group has been replaced by an amide group,



Other natural polysaccharides include pectin in fruits and gums from trees. Sugars other than glucose polymerize. The five-carbon sugars (pentoses) form hemicellulose and make up part of the cell walls in plants.

SUPPLEMENTARY MATERIAL

Proteins are the first class of compounds whose structure was explained on the basis of a helical molecular form. The idea has been well proved by X-ray analysis of natural proteins and of similar, synthetic polyamides. The same idea has been used for nucleic acids. Unfortunately, however, they have a complex double helix that is beyond our ability to fruitfully discuss in this course. See *Supplementary Material* for suggested reference.

Hydrogen bonds are quite important in explaining the properties of polyamides (and of the polysaccharides, too, although this was not brought out when they were discussed). The previous comments (p. 189) about the effect of hydrogen bonds on molecular properties apply to these more complex polymeric substances, but they are more difficult to demonstrate.

Film, BIOCHEMISTRY AND MOLECULAR STRUCTURE,

fits here. See p. 385 for summary.

18-13 Enzymes

This section deals with the importance of limited parts of big molecules. The entire "lock and key" theory of enzyme action requires that there be certain areas to which the substrate molecule fits particularly well. This theory explains many of the observed facts. Until recently, not much else was possible, because the structure of enzymes was not known, but this is changing.

All the enzymes are proteins, and their structures are partly like the helix shown in Textbook Figure 18-9. A single molecule may have more than one helix joined together. These helices

are thought to be joined side by side through covalent —S—S—, or disulfide, bridges.

Lysozyme was the first enzyme whose structure was determined. Figure 18-2 on p. 384 shows the main peptide chain. Each circle represents one of the 129 amino acid residues. The thick bonds serve to indicate portions in the helical shape.

Another enzyme, chymotrypsin is undergoing X-ray study now. This enzyme forms from precursors produced in the pancreas and aids in digesting proteins. It catalyzes the breaking of the polyamide chain.

18-14 Energy Sources in Nature

This section discusses the only example of a cycle that we present. (It is a short version of the Krebs cycle.) Cycle is not a perfect name, since it implies a succession of steps. Actually, we have a set of concurrent reactions which continue to operate because some of the products (CO_2 and H_2O) are removed.

The reactions represented in the cycle are known to be considerably more complex than shown. At least eighteen steps are known, involving thirteen enzymes. The simpler version serves our needs. The student should realize these reactions do not violate the conservation of energy law. Some reactions serve to store energy that is liberated by other reactions. There is no creation of energy by the plant.

Expt. 40, THE PREPARATION OF ESTERS,

can be used anytime after Expt. 39. See p. 232 in the Laboratory Guide.

Supplementary Material

Article

I. Raw, "Enzymes—How They Operate," *Chemistry*, June 1967, p. 9. See also p. 21.

Book

The Cell, Life Science Library, Silver Burdett Co., 1964. Pages 69–74 contain excellent illustrations of the DNA helix and its part in protein synthesis.

Films

A CHEM Study film

For ordering information see the *List of Film Sources* at the back of the Teacher's Guide.

Running Time: 22 minutes

This film was produced with the collaboration of Professor T. A. Geissman, an outstanding chemist specializing

1. SYNTHESIS OF AN ORGANIC COMPOUND

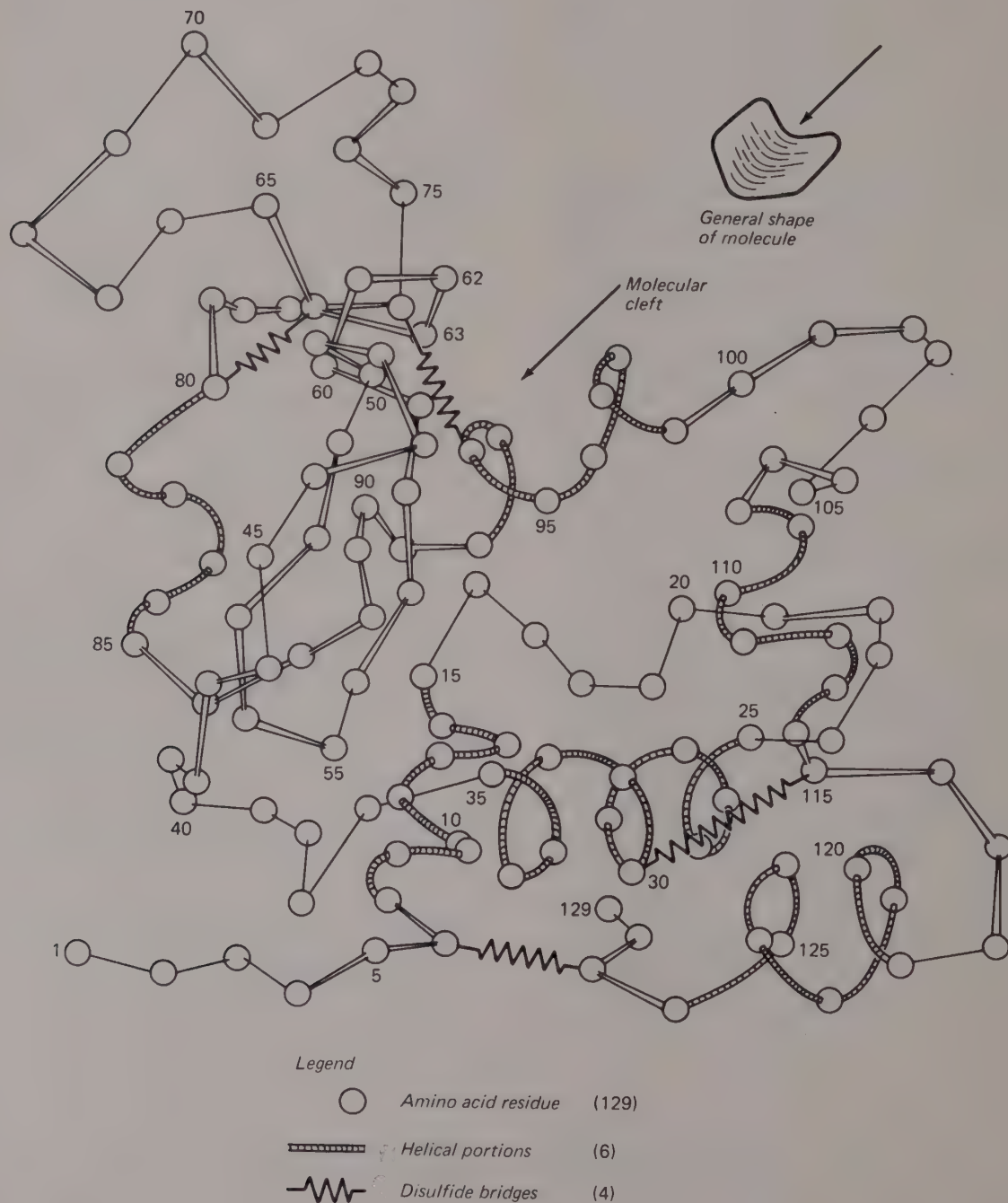


FIGURE 18-2

The structure of lysozyme.

BACKGROUND DISCUSSION

in organic synthesis. The film gives the student an opportunity to view some typical laboratory operations and equipment of organic chemistry. Thus it provides a partial substitute for the student laboratory experience made inaccessible by the expense of equipment and fire hazards. Using the oxidation of an alcohol to a ketone (as discussed on Textbook p. 362), the following laboratory operations are demonstrated:

- (a) refluxing a reaction mixture with temperature control and stirring;
- (b) a liquid-liquid extraction by means of a separatory funnel;
- (c) drying an organic liquid with an anhydrous salt;
- (d) distillation;
- (e) identification by derivative formation;
- (f) melting temperature determination;
- (g) identification by infrared spectrum.

2. MECHANISM OF AN ORGANIC REACTION

A CHEM Study film

Running Time: 20 minutes

Prof. H. Rapoport collaborated in making this film study of the hydrolysis of an organic ester. It shows determina-

tion of the chemical equation, the structures of reactants and products, the fate of each atom of the reactants, and the structure of intermediate molecules. Mass spectrographic detection of an oxygen isotope, ^{18}O , is a critical part of the unraveling story.

3. BIOCHEMISTRY AND MOLECULAR STRUCTURE

A CHEM Study film

Running Time: 22 minutes

The collaborator, Dr. Donald E. Rounds, Pasadena Foundation for Medical Research, Pasadena, California, demonstrates the role of molecular structure in determining biological activity. Correlation of the structure and biological activity of sulfanilamide with a vitamin essential for bacterial growth leads to a more general investigation of the biochemical nature of growth. Paper chromatography is used to separate some of the compounds which make up human cells. It is proposed that compounds similar to those found in cell chromosomes may stop cell growth and thus be useful in controlling cancer. The technique of time-lapse microphotography is used to demonstrate the effect of one such compound, 5-fluorouracil, on cancer cells.

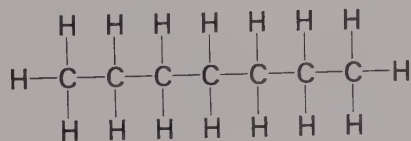
Background Discussion

It is not reasonable to expect anything like "thorough coverage" in this chapter. Concentrate on showing that no new principles are needed for organic chemistry. You might expect the student to learn what data are needed for getting at the structure of a molecular compound and to learn the concept of skeletal integrity. He can also be expected to understand a few reactions of the simple functional groups.

The Large Number of Carbon Compounds

One question that can lead to a discussion of value is: Why do so many compounds of carbon and hydrogen exist, whereas not nearly so many exist for any other pair of elements? The answer would have the following main features. As a result of its electron structure, carbon forms four equivalent bonds joining it to other atoms. These can be other carbon atoms, hydrogen atoms, oxygen, nitrogen, or halogen atoms (and others which are beyond the purpose of our

discussion). This means that not only can long chains of carbon atoms be formed,

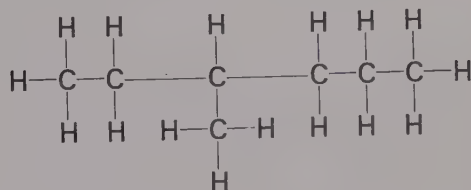


or



heptane

but branching of the chain can occur,

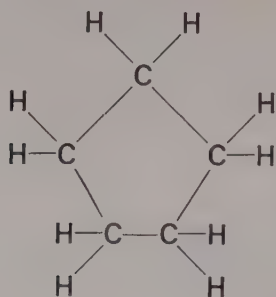


or

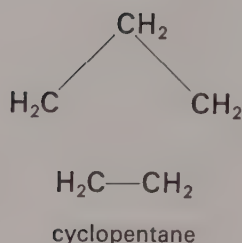


3-methylhexane

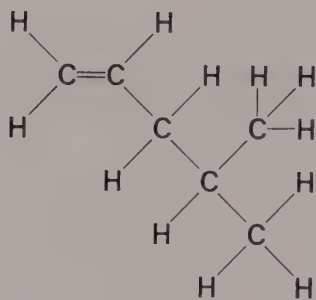
and rings of carbon atoms can exist,



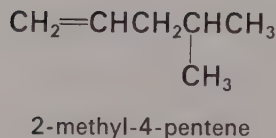
or



Furthermore, *double bonds* occur in many organic compounds;

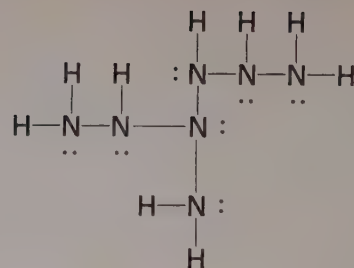


or



Note that only relatively small molecules are discussed. Remind the student that molecules containing up to twenty carbon atoms are common and that there are many still larger ones.

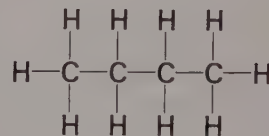
From this start you can lead into the more difficult question: "Why doesn't nitrogen form long chains and branched chains, such as



or, why doesn't silicon form compounds that are the counterparts of the carbon compounds?"

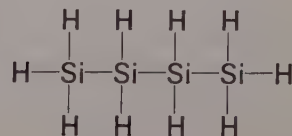
The answers to these reasonable questions are difficult, because such compounds *can* exist but do not because of their great instability. In the complex nitrogen compound shown above, each nitrogen atom contains an unshared pair of electrons (shown as the dots on the N atoms). These are points of attack by electron-seeking reagents (such as acids, which can provide H^+), and, consequently, reactions that lead to the rupture of such chains take place very readily.

On the other hand, in the long-chain carbon compounds, each carbon atom has used all of its valence electrons in bond formation and has a complete (filled) second energy level. Thus the only way for a compound such as butane,



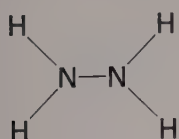
to react is for one of the C—C bonds or one of the C—H bonds to break first. This actually can and does take place; but because of the high energy required to break C—C and C—H bonds these reactions take place either very slowly or at high temperatures (as in the cracking of petroleum).

Why, then, doesn't silicon form stable molecules such as

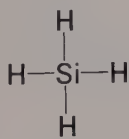


BACKGROUND DISCUSSION

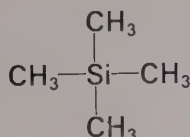
Silicon does indeed form such compounds, but they are very unstable; silicon (in the third row) has available $3d$ orbitals, and even though in SiH_4 , for example, the $3s$ and $3p$ orbitals are completely used in bond formation, reagents that have unshared electrons (such as H_2O) can form a fifth bond to the silicon atom, and reactions that give other products can then occur. It should be pointed out that the simple analogs of carbon compounds are well known for nitrogen and silicon:



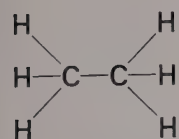
hydrazine



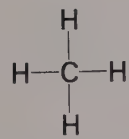
silane



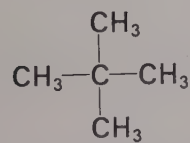
tetramethyl silane



ethane



methane

2,2-dimethylpropane
or neopentane

Sources of Carbon Compounds

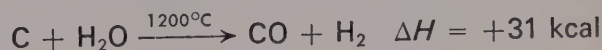
The following explains the main routes for the chemical use of coal and oil. We usually regard coal, oil, wood, and natural gas as fuels. This is, of course, their chief use; but they serve as the source of the carbon in organic compounds of all kinds.

How is the carbon of coal or petroleum converted into the compounds that serve as starting materials for chemical synthesis? Let us take coal as an example and see how it is used. Initially, coal is heated to produce coal tar (and other fractions) and coke.

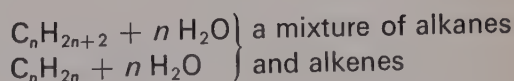
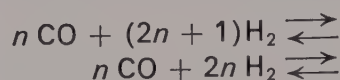
Coal tar is a mixture of many compounds; among the industrially important ones are benzene, naphthalene, phenol, and toluene.

Coke is used as a source of carbon in at least two routes to synthetic carbon compounds.

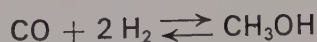
1. Water gas is prepared by the reaction of coke with steam at a high temperature (recall the use of this reaction in Chapter 7).



In the Fischer-Tropsch process for the manufacture of fuels, water gas is transformed (with high temperature, high pressure, and a catalyst) into a mixture of hydrocarbons.

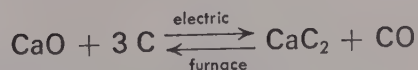


The conversion of water gas into methanol is also an important industrial process:



Either hydrocarbons or alcohols result from different catalysts or conditions.

2. Acetylene is prepared, starting with coke, by way of calcium carbide:



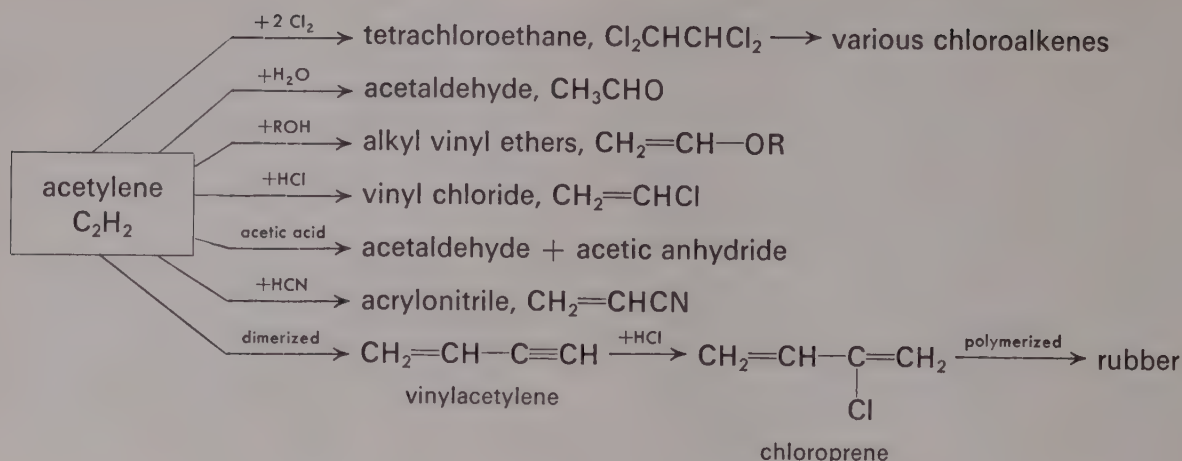
$$\Delta H = +110 \text{ kcal}$$

Acetylene is produced by treating the calcium carbide with water:



$$\Delta H = -30 \text{ kcal}$$

A great variety of valuable products is prepared from acetylene:



The vinyl compounds ($CH_2=CH-X$) are monomers used in synthetic plastic and fiber production.

From the foregoing examples it can be seen that a number of very important industrial organic chemicals can be produced by means of a few simple processes. These processes use raw materials (coal, coke, natural gas) that are cheap and very abundant. Thus acetylene, methanol, acetic acid, acetaldehyde, and vinyl compounds can be produced in vast quantities. The organic chemist can transform these into countless other compounds.

Petroleum-derived Chemicals

Petroleum is the remaining large source of carbon. Among the products of the petroleum industry are the simple alkenes: ethylene, propylene, and the butenes. These are the raw materials for making alcohols, ketones, and esters.

It should be emphasized that economic considerations play an important part in shaping the direction of chemical development. A good deal of the effort of industrial chemists consists in finding ways to use the enormous amounts of the simple starting materials that are produced from the abundant sources of carbon.

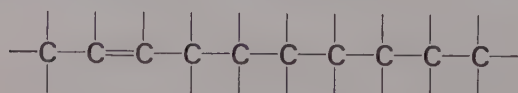
Answers to Exercises and Problems

Exercise 18-1

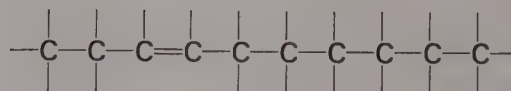
Draw structural formulas for the four other possible isomers of $C_{10}H_{20}$. Why are there not nine?

Answer

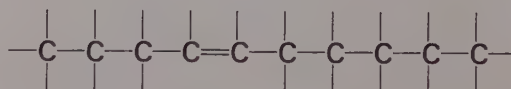
The isomer in the Textbook, p. 357, is 1-decene.



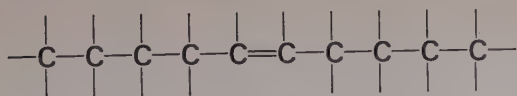
2-decene



3-decene



4-decene

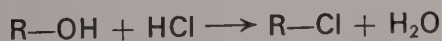


5-decene

There are no more straight chain decene isomers because there are no more *different* ways to place a double bond. The students will propose 6-decene, but it is just like 4-decene, 7 is like 3, and so on.

Exercise 18-2

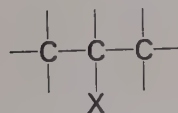
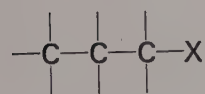
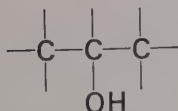
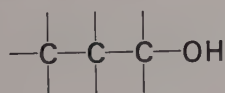
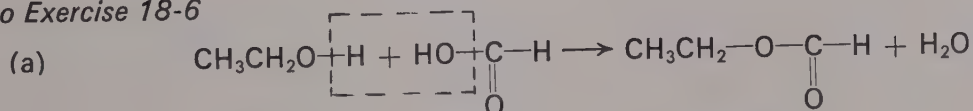
Write the equation for the general reaction between alcohols and HCl. Use $-R$ to represent the hydrocarbon part of the molecules.

Answer**Exercise 18-3**

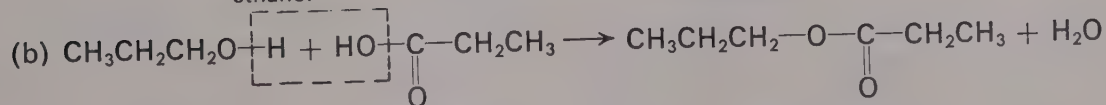
Give the structural formula for two derivatives of propane.

Answer

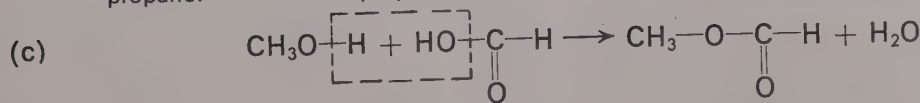
Hydroxide and halogen derivatives are all the student has seen so far. The most likely formulas are

*Answer to Exercise 18-6*

ethanol formic acid ethyl formate



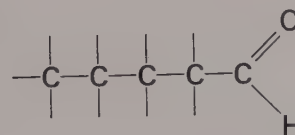
propanol propionic acid propyl propionate



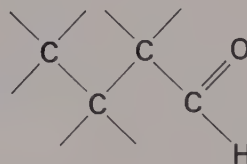
methanol formic acid methyl formate

Exercise 18-4

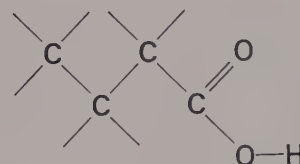
Write the formula of the aldehyde made from normal pentane.

Answer**Exercise 18-5**

Butanol is an alcohol with the structural formula, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$. If it is oxidized carefully, an aldehyde called butyraldehyde is obtained. Vigorous oxidation gives an acid called butyric acid. Draw structural formulas of these compounds like those shown in Figures 18-1 and 18-2.

Answer

butyraldehyde



butyric acid

Exercise 18-6

Write equations for the reaction of (a) ethanol and formic acid; (b) propanol and propionic acid; (c) methanol and formic acid. Name the esters produced.

Exercise 18-7

Glucose, a sugar simpler than sucrose, has a molar mass of 180 g and empirical formula CH_2O . What is its molecular formula?

Answer

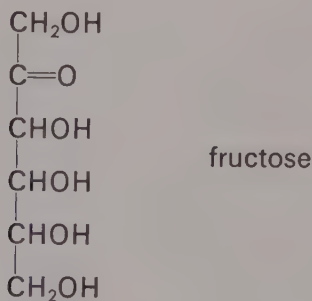
The empirical molar mass of CH_2O is 30 g.

Thus the glucose formula contains $\frac{180}{30}$, or 6 empirical formulas. The glucose formula is $\text{C}_6\text{H}_{12}\text{O}_6$.

Exercise 18-8

Draw a structural formula for the fructose molecule (remember that fructose is an isomer of glucose).

Answer



Exercise 18-9

At equilibrium in a 0.1 M solution of glucose in water, only 1% of the glucose is in the straight chain form. What is K for the reaction: chain $\rightleftharpoons$ ring?

Answer

The equilibrium reaction can be expressed

chain $\rightleftharpoons$ ring

$$K = \frac{[\text{ring}]}{[\text{chain}]} = \frac{0.099}{0.001} = 99$$

The ring form is favored.

Exercise 18-10

The monomer unit in starch and that in cellulose each has the empirical formula $\text{C}_6\text{H}_{10}\text{O}_5$. These units are about 5.0 Å long. Approximately how many units occur and how long are the molecules of cellulose and of soluble starch?

Answer

The empirical molar mass of $\text{C}_6\text{H}_{10}\text{O}_5$ is 162.

For starch,

$$\frac{4000}{162} = 25 \text{ glucose units}$$

For cellulose,

$$\frac{600,000}{162} = 3700 \text{ glucose units}$$

length of starch molecule:

$$25 \text{ units} \times 5 \text{ Å/unit} = 125 \text{ Å}$$

length of cellulose molecule:

$$3700 \text{ units} \times 5 \text{ Å/unit} = 19,000 \text{ Å}$$

Problem 1

How much ethanol can be made from 50 grams of ethyl bromide? What assumptions do you make in answering this question?

Answer

The maximum possible yield of ethanol that can be obtained is calculated on the assumption that the hydrolysis



can be carried to completion and that all of the ethyl group in the starting material is recovered in the ethanol. That is, *one mole* of ethyl bromide gives *one mole* of ethanol. In practice, some $\text{CH}_3\text{CH}_2\text{Br}$ is always found to exist in the equilibrium mixture. The molar masses are: ethyl bromide, 108.9; ethanol, 46.0 grams.

$$50 \text{ g ethyl bromide} \times \frac{1}{108.9 \text{ g/mole}} = 0.46 \text{ mole}$$

$$0.46 \text{ mole ethyl bromide} \times \frac{1 \text{ mole ethanol}}{1 \text{ mole ethyl bromide}} = 0.46 \text{ mole ethanol}$$

$$0.46 \text{ mole ethanol} \times \frac{46.0 \text{ g}}{\text{mole}} = 20.4 \text{ g ethanol}$$

or

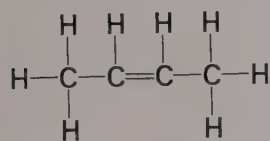
20 g ethanol

Problem 2

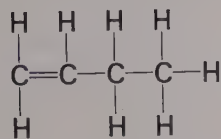
Give the empirical formula, the molecular formula, and draw the structural formulas of the isomers of butene. This hydrocarbon contains four carbon atoms and one double bond.

Answer

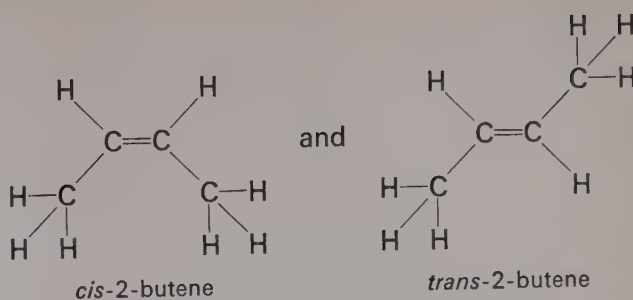
The empirical formula is CH_2 ; the molecular formula is C_4H_8 .



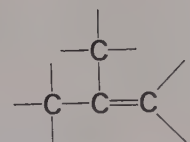
2-butene



1-butene



A third isomer is



2-methylpropene

The isomer 2-butene exists in two forms

Problem 3

Ethane, C_2H_6 , reacts with chlorine to substitute first one chlorine for hydrogen, then two, and so on until C_2Cl_6 is formed. How many different ethane derivatives form in this series of reactions?

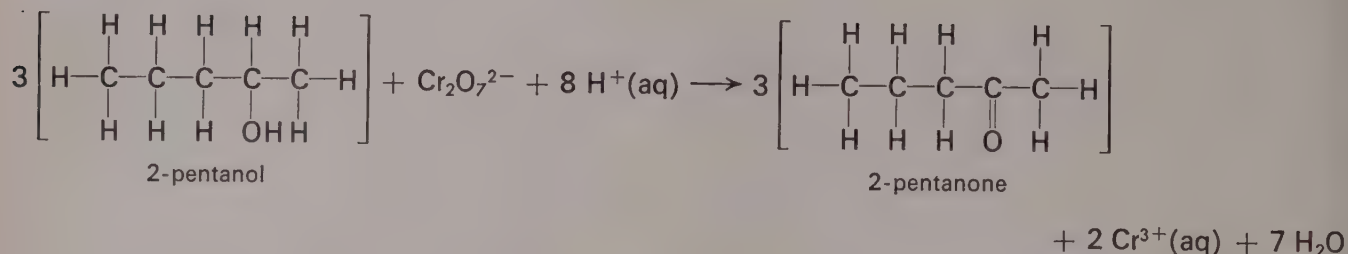
Answer

The answer is most compactly given in a table. There are 9 chloroethane derivatives.

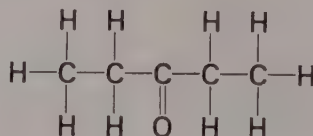
Number of Chlorines	Molecular Formula	Structural Formulas
1	$\text{C}_2\text{H}_5\text{Cl}$	$\begin{array}{c} & \\ -\text{C} & -\text{C}-\text{Cl} \\ & \end{array}$
2	$\text{C}_2\text{H}_4\text{Cl}_2$	$\begin{array}{cc} \begin{array}{c} & \\ -\text{C} & -\text{C}-\text{Cl} \\ & \\ & \text{Cl} \end{array} & \begin{array}{c} & \\ -\text{C} & -\text{C}- \\ & \\ \text{Cl} & \text{Cl} \end{array} \end{array}$
3	$\text{C}_2\text{H}_3\text{Cl}_3$	$\begin{array}{cc} \begin{array}{c} & \\ -\text{C} & -\text{C}-\text{Cl} \\ & \\ & \text{Cl} \end{array} & \begin{array}{c} & \\ -\text{C} & -\text{C}-\text{Cl} \\ & \\ \text{Cl} & \text{Cl} \end{array} \end{array}$
4	$\text{C}_2\text{H}_2\text{Cl}_4$	$\begin{array}{cc} \begin{array}{c} & \\ -\text{C} & -\text{C}-\text{Cl} \\ & \\ \text{Cl} & \text{Cl} \end{array} & \begin{array}{c} \text{Cl} & & \text{Cl} \\ & & \\ -\text{C} & - & \text{C}-\text{Cl} \\ & & \\ \text{Cl} & & \text{Cl} \end{array} \end{array}$
5	C_2HCl_5	$\begin{array}{c} \text{Cl} \\ \\ \text{Cl}-\text{C} & - & \text{C}-\text{Cl} \\ & & \\ \text{Cl} & & \text{Cl} \end{array}$
6	C_2Cl_6	$\begin{array}{c} \text{Cl} \\ \\ \text{Cl}-\text{C} & - & \text{C}-\text{Cl} \\ & & \\ \text{Cl} & & \text{Cl} \end{array}$

Problem 4

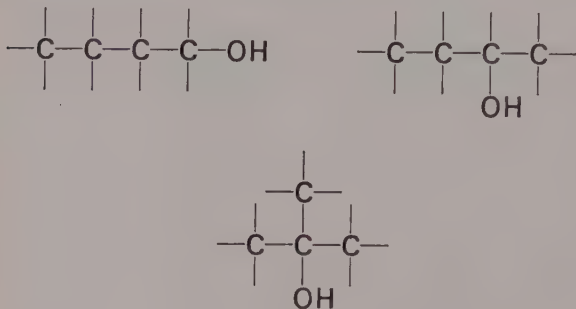
Write the balanced equation for the production of pentanone from pentanol, using dichromate ion as the oxidizing agent.

Answer

The same equation applies if 3-pentanol is used, giving 3-pentanone,

**Problem 5**

Knowing the possible oxidation products of ethanol and 2-propanol, predict the oxidation products of:

**Answer**

1-Butanol can give butyraldehyde, next butyric acid, and then CO_2 and H_2O .

2-Butanol can give butanone, then CO_2 and H_2O .

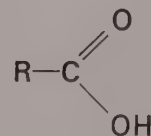
The third isomer (*tert*-butanol or 2-methyl-2-propanol) does not give any four-carbon oxidation products.

Problem 6

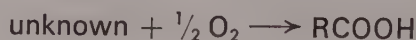
One mole of an organic compound is found to react with $\frac{1}{2}$ mole of oxygen to produce an acid. To what class of compounds does this starting material belong?

Answer

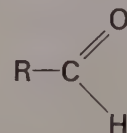
In terms of the general formula, the acid can be represented as



Since the reaction is stoichiometrically defined in the problem as



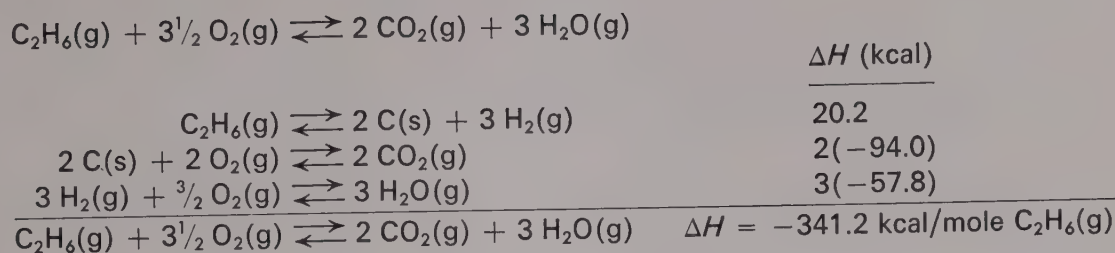
the starting material must be the aldehyde.



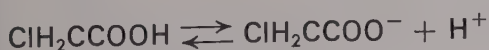
Problem 7

Using the information given in Table 11-2, determine

the reaction heat per mole of $\text{C}_2\text{H}_6(\text{g})$ for the complete combustion of ethane.

Answer**Problem 8**

An aqueous solution containing 0.10 mole/liter of chloroacetic acid, ClH_2CCOOH , is tested with indicators and the concentration of $\text{H}^+(\text{aq})$ is found to be $1.2 \times 10^{-2} \text{ M}$. Calculate the value of K_A (if necessary, refer back to Section 14-8). Compare this value with K_A for acetic acid—the change is caused by the substitution of a halogen atom near a carboxylic acid group.

Answer

$$K_A = \frac{[\text{H}^+][\text{ClH}_2\text{CCOO}^-]}{[\text{ClH}_2\text{CCOOH}]}$$

In an aqueous solution of pure acid,

$$[\text{H}^+] = [\text{ClH}_2\text{CCOO}^-] = 1.2 \times 10^{-2}$$

$$K_A = \frac{(1.2 \times 10^{-2})^2}{(0.10 - 0.012)} = 1.6 \times 10^{-3}$$

The acetic acid dissociation constant is

$$K = 1.8 \times 10^{-5}$$

The increased acid strength of chloroacetic acid is considered to result from chlorine, with its high ionization energy, pulling electrons from the carboxyl group, weakening the O—H bond.

Problem 9

Give simple structural formulas of

- an alcohol,
- an aldehyde, and
- an acid,

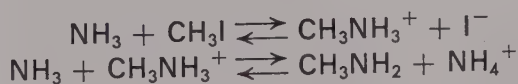
each derived from methane; from ethane; from butane; from octane.

Answer to Problem 9

Alcohol	Aldehyde	Acid
CH_3OH	HCHO	HCOOH
$\text{C}_2\text{H}_5\text{OH}$	CH_3CHO	CH_3COOH
$\text{C}_4\text{H}_9\text{OH}$	$\text{C}_3\text{H}_7\text{CHO}$	$\text{C}_3\text{H}_7\text{COOH}$
$\text{C}_8\text{H}_{17}\text{OH}$	$\text{C}_7\text{H}_{15}\text{CHO}$	$\text{C}_7\text{H}_{15}\text{COOH}$

Problem 10

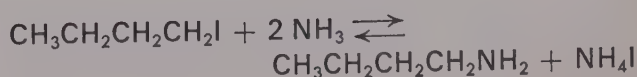
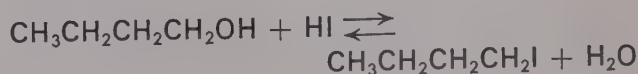
Write the equations for the preparation of methylamine from methyl iodide.

Answer

as given in Section 18-4.

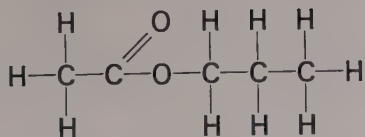
Problem 11

Show a two stage synthesis for the formation of butylamine starting with *n*-butyl alcohol, HI and NH_3 .

Answer

Problem 14

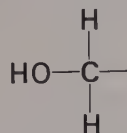
Given the structural formula



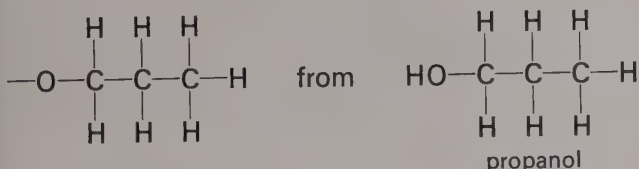
for an ester, write the formula of the acid and the alcohol from which it might be made.

Answer

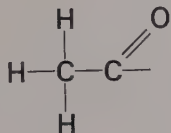
An alcohol has a group of the type



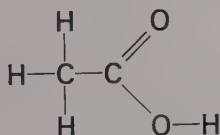
hence that part of the ester derived from the alcohol is the propyl group,



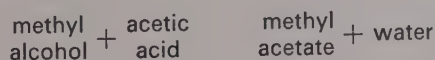
The remainder,



came from acetic acid,

**Problem 15**

In the preparation of methyl acetate, the yield of ester is rather low at equilibrium. What can be done to increase the yield? Study the equation and apply Le Chatelier's Principle.



Answer

Remove water as it is produced using a drying agent such as H_2SO_4 . Increase the concentration of one of the reagents.

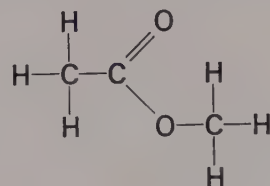
Problem 16

How much acetamide can be made from 3.1 grams of methyl acetate? See equation on page 362. Assume the ester is completely converted.

Answer. 2.5 grams acetamide

Answer

The molar mass of methyl acetate,



is

$$3(12) + 6(1) + 2(16) = 36 + 6 + 32 = 74 \text{ g/mole.}$$

$$3.1 \text{ g methyl acetate} \times \frac{1}{74 \text{ g/mole}} = 0.042 \text{ mole}$$

$$(0.042 \text{ mole methyl acetate}) \left(\frac{1 \text{ mole amide}}{1 \text{ mole acetate}} \right) = 0.042 \text{ mole acetamide}$$

$$0.042 \text{ mole amide} \times \frac{59 \text{ g}}{\text{mole}} = 2.48 \text{ or } 2.5 \text{ g acetamide}$$

Problem 17

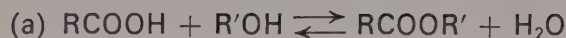
An ester is formed by the reaction between an acid, RCOOH , and an alcohol, R'OH , to form an ester RCOOR' and water. The reaction is carried out in an inert solvent.

- Write the equilibrium relation among the concentrations, including the concentration of the product water.
- Calculate the equilibrium concentration of the ester if $K = 10$ and the concentrations *at equilibrium* of the other constituents are:
 $[\text{RCOOH}] = 0.1 \text{ M};$
 $[\text{R'OH}] = 0.1 \text{ M};$
 $[\text{H}_2\text{O}] = 1.0 \text{ M}.$

- Repeat the calculation of part (b) if the equilibrium concentrations are:

$$\begin{array}{l}
 [\text{RCOOH}] = 0.3 \text{ M}; \\
 [\text{R'OH}] = 0.3 \text{ M}; \\
 [\text{H}_2\text{O}] = 1.0 \text{ M}.
 \end{array}$$

Answer



$$K = \frac{[\text{RCOOR}'] [\text{H}_2\text{O}]}{[\text{RCOOH}] [\text{R}'\text{OH}]}$$

$$(b) 10 = \frac{[\text{RCOOR}'] (1.0)}{(0.1)(0.1)}$$

$$[\text{RCOOR}'] = \frac{10(0.1)(0.1)}{1.0} = 0.1 \text{ M}$$

$$(c) 10 = \frac{[\text{RCOOR}'] (1.0)}{(0.3)(0.3)}$$

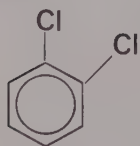
$$[\text{RCOOR}'] = \frac{10(0.3)(0.3)}{1.0} = 0.9 \text{ M}$$

Suppose we have a small amount of a valuable acid that we wish to convert into the methyl ester. If a very large excess of methanol is used, the conversion of the acid into the ester will be nearly complete. The disadvantage of using one reactant in large excess is that the percentage of *this* reactant that is converted to ester is small. But when the alcohol is, for example, the inexpensive and easily available methanol, this is not an important consideration and is far outweighed by the advantage of practically *complete* conversion of the other reagent (the acid) into ester.

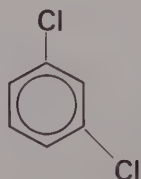
Problem 18

There are three isomers of dichlorobenzene (empirical formula $\text{C}_6\text{H}_4\text{Cl}_2$). Draw the structural formulas of the isomers.

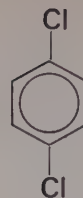
Answer



1,2-dichlorobenzene
or
orthodichlorobenzene



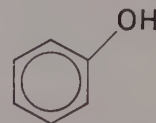
1,3-dichlorobenzene
or
metadichlorobenzene



1,4-dichlorobenzene
or
paradichlorobenzene

Problem 19

Consider the compound phenol,



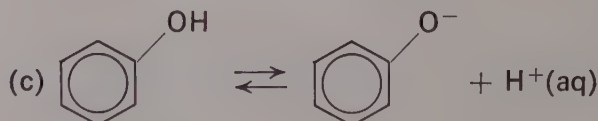
- Predict the angle formed by the nuclei C, O, H. Explain your choice in terms of the orbitals used by oxygen in its bonds.
- Predict qualitatively the boiling temperature of phenol. (The boiling temperature of benzene is 80°C .) Explain your answer.
- Write an equation for the reaction of phenol as a proton donor in water.
- In a 1.0 M aqueous solution of phenol,

$$[\text{H}^+] = 1.1 \times 10^{-5}$$

Calculate K_A .

Answer

- Since the oxygen uses p orbitals in its bonding, the two bonds should form an angle near 90° . This angle should be about 105° , based on the value for water and alcohols. The functional group attached to $-\text{OH}$ has little effect on the bond angle.
- The boiling temperature of phenol should be greater than that of benzene because it can form hydrogen bonds, whereas benzene cannot. The observed value is 182°C .



or



$$(d) K = \frac{[\text{C}_6\text{H}_5\text{O}^-] [\text{H}^+]}{[\text{C}_6\text{H}_5\text{OH}]}$$

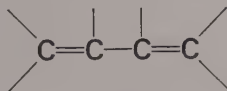
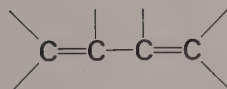
$$[\text{H}^+] = [\text{C}_6\text{H}_5\text{O}^-] = 1.1 \times 10^{-5} \text{ M}$$

$$[\text{C}_6\text{H}_5\text{OH}] = 1.0 - (1.1 \times 10^{-5}) \approx 1.0 \text{ M}$$

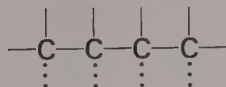
$$K = \frac{(1.1 \times 10^{-5})^2}{1.0} = 1.2 \times 10^{-10}$$

Problem 20

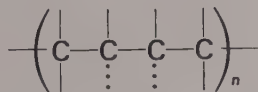
Work out a possible structural formula for the polymer of 1,3-butadiene,

**Answer**

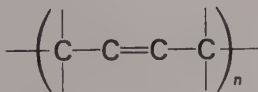
can be imagined to form an intermediate



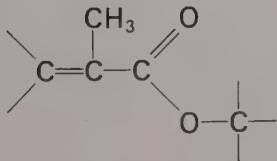
where dotted lines indicate half-filled orbitals. Such a molecule could join others to give



and finally the two unsatisfied bonding capacities join.

**Problem 21**

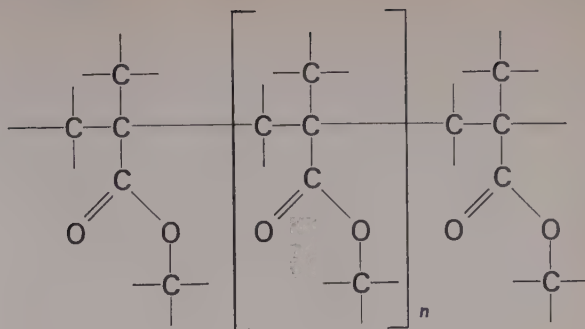
Lucite is an addition polymer of methylmethacrylate, shown below



Draw a portion of the Lucite structure.

Answer

Redrawing the monomer, opening and joining the double bonds gives

**Problem 22**

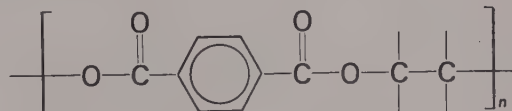
What types of bonds would you expect to bind the very long polyethylene molecules to each other? The long Nylon molecules to each other? Which polymer would you expect to melt at the lower temperature?

Answer

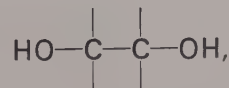
Polyethylene molecules would be held together by van der Waals bonds or forces. Nylon molecules are hydrogen bonded. Polyethylene should melt first. The experimental values agree: polyethylene, 110°C; Nylon, 270°C.

Problem 23

Dacron is a polyester made in a way similar to Nylon. The structure is



What alcohol is used in making Dacron?

Answer

ethylene glycol or 1,2-dihydroxyethane. This answer is contained in Section 18-8.

Problem 24

Nylon and Dacron are made from monomers containing two functional groups per molecule. What type of polymers might result if a monomer had three or more functional groups?

Answer

Long molecules with covalently bonded chains

would form and still have functional groups to react. Such reaction would interlock the molecules into sheets or three-dimensional networks. Such polymers might be like network solids: high melting, low solubility, hard. Bakelite is such a polymer, and some polyester polymers have such characteristics.

Problem 25

Account for the fact that starch, a glucose polymer, is readily assimilated as food by humans but cellulose, also a glucose polymer, is not.

Answer

Starch is a polymer of the α form of glucose and cellulose is made from the β form. Humans cannot digest the β form polymer.

General Comments on Remaining Chapters

Beyond Chapter 18 the Textbook material and laboratory work have a new character. New principles are rarely encountered; instead the usefulness of those already studied is demonstrated in several new areas of chemistry. The Textbook and experiments are a deliberate review of basic concepts through use.

Because of the change described, there is less need to adhere to a particular order of Textbook and lab topics. You should pick them to suit your class and the time available, taking full advantage of the chance to review. Experiments 39–44 do not have the close connection to a given section of the Textbook that has characterized the first 38 experiments.

The Halogens



Intent and Approach

This chapter is the first of two dealing with selected portions of the Periodic Table. It focuses on the halogens, column VII, and conveys the similarities and systematic differences displayed by these elements. In directing the study of this chapter, encourage students to concentrate on these similarities and differences. Also encourage them to examine the chemical behavior

of the group with these regularities and differences in mind.

Chapter 19 also represents a shift, which continues for the remainder of the course, from an emphasis on principles to an emphasis on the descriptive side of chemistry. Bring the principles in as much as possible, and relate them to the description of the halogens.

Outline

The preparation and properties of halogens are presented (19-1, 19-2).

Oxidation-reduction is the principal reaction (19-2).

The positive oxidation states, oxyacids, and oxyanions of halogens are discussed in Sec-

tion 19-4.

Some uses of halogen compounds (19-5) and particularly photography (19-6) are covered.

A concluding section deals with the exceptional qualities of fluorine (19-7).

New Concepts

This is a descriptive chapter whose primary intent is not to introduce new concepts, but to reinforce and apply some already studied.

Familiar concepts which should be applied are:

1. Structure of matter (electron configuration and molecular shape).

2. Oxidation-reduction.
3. Net equations for reactions.
4. Equilibrium.
5. Energy in reactions.
6. Acids and bases.
7. Species in aqueous solutions.

SCHEDULE AND RELATED MATERIAL

Suggested Time: 4 days

Text Section	Topic and Other Work	Exercise	Problems		
			Easy	Medium	Hard
19-1	Preparation and Properties of Halogens	1	2, 3	1, 4	6
19-2	Sizes of Halogen Atoms and Ions		10	7, 9, 11	5
19-3	Oxidation-Reduction <i>Film:</i> Bromine—Element from the Sea				8, 12, 13
19-4	Expt. 41, Electrolysis of KI Positive Oxidation States of Halogens: The Oxyacids		14	15-19	20
19-5	Importance of Halogens and their Compounds				
19-6	Photography				
19-7	Special Remarks on Fluorine				

Expt. 42, Some Chemistry of Iodine, can be used anytime after Expt. 41.

Development

Introduction

Keep in mind that the halogens are not unknown to the student. A section of Chapter 7 (pp. 115-118, Textbook) is specifically devoted to them. Textbook Table 7-9 enumerates many of the empirical properties, and these are also discussed in the section. A review of that section along with the study of Sec. 19-1 is a good way to initiate this chapter.

19-1 Preparation and Properties of the Elements

19-2 The Sizes of Halogen Atoms and Ions

One striking thing about the halogens is that they are all colored. This is a good time to point out that most nonmetallic elements (again, the

noble gases are exceptions) are colored. Note the following portion of the Periodic Table. The colors probably result from the covalent bonding present and the position of the electron energy levels. The *Background Discussion* contains more information.

This section contrasts atomic and ionic radii; how these radii change in going down the column; and how they are related to melting temperature, boiling temperature, bond energy, and dissociation constants (Table 19-1 in the Textbook). Use Problems 3, 4, and 5 to emphasize the regularity of increase in atomic and ionic size, and also the regularity of melting and boiling temperature increases. Be sure to make the distinction that covalent radii show the size "within a molecule"—that is, for atoms bonded together. Van der Waals radii show the distance of approach "between molecules"—that is, how close two nonbonded atoms can come.

					He colorless
B black, brown	C black	N colorless	O (blue)*	F pale yellow-green	Ne colorless
	Si gray	P red, white, plus others	S yellow	Cl yellow-green	Ar colorless
			Se red, gray	Br red-brown	Kr colorless
				I violet	Xe colorless

* Ozone is deep-blue—almost black as a pure liquid.

19-3 The Oxidation-Reduction Properties for the Halogens

You can add some vitality to these sections by demonstrating the statements at the beginning of the Section. The best practice is to have the students work out the answers ahead of time, using E° values. Problem 9 is specifically for such use. With this background, consult H. N. Alyea and F. B. Dutton, *Tested Demonstrations in Chemistry*, Div. Chem. Education, ACS, Easton, Pennsylvania (p. 44) for details. Make the demonstration short, showing $\text{Cl}_2 + \text{Br}^-$ and $\text{Br}_2 + \text{I}^-$.

The series of steps postulated in Table 19-2 are an example of a Born-Haber cycle. Such cycles are useful for breaking a process into imagined component parts. It is also used to calculate the energy required in one particular step if that for all others is known. This is the usual way to get values for electron capture, because electron affinity measurements are difficult to make. The *trend* of values is probably the important aspect to look at. The exact values are not crucial.

Film, BROMINE—ELEMENT FROM THE SEA,
fits here. See p. 404 for summary.

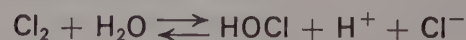
Expt. 41, THE ELECTROLYSIS OF AQUEOUS POTASSIUM IODIDE,

fits here. See p. 238 in the Laboratory Guide.

19-4 Positive Oxidation States of Halogens: The Oxyacids

This section offers a chance to employ the student's background on equilibrium, acidity, bonding, and structure. Show him how the things he studied as separate parts of chemistry come together when the chemistry of a group of elements is studied.

The equilibrium reaction



is common in swimming pools. The equilibrium constant is about 3×10^{-4} . The oxyacids have these values of K_A :

HOCl	3.6×10^{-8}
HOCIO	1.1×10^{-2}
HOCIO ₂	~ 3
HOCIO ₃	large

The more or less tetrahedral structure of the halogen oxyacids fits with the shape found for other sp^3 bonded compounds. The electrons

DEVELOPMENT

needed to form the various bonds all find appropriate vacant orbitals.

You can make a point about oxidation numbers here. Although we attach little importance to the particular values chemists have chosen to use, the fact that an element *changes* oxidation number *is* important. It means there is a different arrangement of electrons around the atom and, thus, that different properties and behavior are to be expected.

Expt. 42, SOME CHEMISTRY OF IODINE,
can fit here. See p. 240 in the Laboratory Guide.

19-5 The Importance of the Halogens and Their Compounds

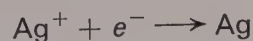
19-6 Photography

The first of these sections merely lists a few of the important, commercial halogen chemicals. The second section gives another opportunity to show how the principles studied earlier bear on a practical example. Photography makes use of kinetics (in exposure, developing, and fixing), oxidation-reduction (developing), polymerization (making the film), and energy interacting with matter (exposure).

Silver halides are not the only chemicals sensitive to light. Most organic dyes fade; iron compounds are changed by light in the blueprint process; some chemicals in human skin are modified by light. In most of these cases, the *yield*, that is, the number of atoms in the changed state after exposure and development per quantum of light, is very low. Hence intense light is required. Silver halides have a low yield on exposure. Only a few silver atoms are activated by the light. But in the development step, a huge amplification results because the activated atoms act as nuclei for still more reduced silver atoms. In the finished negative there are about 10^9 atoms of silver for each one actually activated by light. This large amplification gives modern film an amazing sensitivity. The energy needed

for a single silver crystal is about 10^{-11} erg or 2×10^{-22} kcal! Such an amount of energy would fall on one square foot of the earth during a 30-second exposure to a candle on the moon!

The exact reason all the silver atoms collect at a few places on the halide crystal is not known. But both electrons and Ag^+ ions are mobile in the crystal. In addition, the equilibrium reaction



is very much in favor of reactants *if* the silver atom is isolated. Silver atoms are not stable in the halide crystal. If atoms form, they break up again at room temperature. It is thought that the small amount of sulfur needed for maximum sensitivity helps stabilize the first few silver atoms that begin the crystal formation.

Some idea of the rigid control required on chemical purity is gained from the following facts. Tin or mercury degrades film if as much as one part per million is present. *But* one or two parts *per billion* act as a desirable sensitizer. Some of the things added to film (and their purpose) are listed below.

- hardener—to strengthen the gelatin—aldehydes or alums
- antifoggants—to cut the reflected exposure around a true exposure spot—bromides, benzotriazole
- sensitizers—to increase sensitivity—Au, Sn, salts
- stabilizers—to delay changes in storage

There are two major theories as to why a developer reduces Ag^+ more rapidly in the presence of metallic silver than in its absence. That is, why does the silver at first “grow” at a few spots and not all over as it will eventually? One theory considers it to be an electrochemical process. The silver takes an electron from the developer molecule and transmits it to a silver ion. In the other theory, the developer and silver ion first form a complex which later deposits a silver atom on the developing crystal. There is not yet available an experiment to decide between these alternatives.

19-7 Special Remarks on Fluorine

This section is devoted to the uniqueness of fluorine. Hydrogen bonding has been encountered before, in relation to water and ethyl alcohol. Point out that F^- is a very strong base. Use the fact that HF is mentioned as a polar solvent to

remark that liquid ammonia and acetic acid are also polar solvents in which an acid-base system of proton donation and acceptance can exist. Relate this to any discussion you might have had on this point in the acid-base chapter.

Supplementary Material

Film

For ordering information see the *List of Film Sources* at the back of the Teacher's Guide.

BROMINE—ELEMENT FROM THE SEA

CHEM Study Films

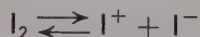
Running Time: 22 minutes

This film, made in collaboration with Dr. L. J. Hollenberg and Dr. J. E. Magner, first demonstrates reactions of Br_2 with metals and nonmetals. Then a laboratory preparation of Br_2 is developed, showing the oxidation-reduction reactions. Finally, the same principles are shown in action in a commercial plant which extracts Br_2 from seawater.

Background Discussion

Positive Oxidation States

There is some evidence, especially for iodine, that in some compounds the halogens may actually have positive ionic charges. For instance, a solution of I_2 in benzophenone (and other organic solvents) conducts an electric current. This can be explained by some dissociation to ions:



In addition, iodine forms saltlike compounds such as ICN (iodine cyanide) and INCO (iodine cyanate) as well as I^{3+} compounds.

$I(C_2H_3O_2)_3$	iodine acetate
$I_2(SO_4)_3$	iodine sulfate
$I(IO_3)_3$	iodine iodate

are the oxyanions given in the Textbook (IO_3^- , ClO_4^- , etc.) and the compounds of the halogens with each other (including ICl, IF_5 , ClF_3 , and several others).

The Oxygen Compounds of Halogens

The oxyacids discussed in the Textbook are like the "common" acids in that they form salts and anhydrides. Some examples are:

Anhydride	Acid	Salt
SO_3	H_2SO_4	M_2SO_4
N_2O_5	HNO_3	MNO_3
Cl_2O	$HClO$	$MClO$
Cl_2O_3	$HClO_2$	$MClO_2$
Cl_2O_5	$HClO_3$	$MClO_3$
Cl_2O_7	$HClO_4$	$MClO_4$

All these chlorine oxides are known (but are very unstable); the acids exist in solution, but only perchloric acid has been isolated. The salts

In many compounds, however, the positive character of the halogens is largely a matter of the arbitrariness of oxidation number. The compounds are largely covalent in bonding. Examples

have all been prepared as crystalline solids.

The oxides of the other halogens are not so numerous, at least at our present state of knowledge. This is partly a result of their instability, which means they are not well known. The regularity of the chlorine compounds and the relation between them and well-known systems can be used to show the organization achieved by the Periodic Table.

The Color of Inorganic Compounds

Most nonmetallic elements are colored (see p. 401). Such colors result from the absorption of part of the white light striking the substance. These bands (and similar, invisible ones in the ultraviolet region) occur when electrons absorb the correct size energy quantum to move to another level. The quantum is used to effect the movement; whatever color corresponds to that quantum size disappears. The substance will then have a complementary color.

There appears to be a connection between covalent bonding and color. Pauling (*The Nature of the Chemical Bond*, p. 105 ff.) gives a table relating covalent character and color for a number of sulfides and halides of eleven metals. In each case, where there is more than about 75% covalent character, the substances are colored. In fact, the color is deeper when there is a larger percent of covalent bonding.

Color also seems to be more common for ions or atoms that have high polarizability—that is, whose electron symmetry is easily deformed by the electric field of another atom or ion. Larger atoms, with their less strongly held outer electrons, tend to have high polarizability. These factors fit the elemental halogens quite well. They are covalently bonded, the larger atoms have deeper color, and their polarizability follows accordingly.

The blue color listed for oxygen is probably due to some other cause, although it, of course, appears blue because part of the light striking it is absorbed. An oxygen molecule does not have a simple, covalent double bond. Evidence, mainly its paramagnetic and spectroscopic be-

havior, suggests that there are two unpaired electrons in each O_2 . The unusual electron structure probably contains appropriate levels, such that the red light is absorbed and the remaining light is blue. The color of metals depends on different, more complex electronic phenomena and is best omitted from discussion.

Photography

One of the outstanding recent developments in photography has been the Polaroid quick development film systems. The black-and-white photographs are fairly simple. Basically they are as explained in Section 19-6. The novelty in this system is in the development of film right at the camera. In a schematic way we can say the film has three layers: a negative layer containing Ag halide crystals and molecules which can potentially develop the exposed silver after activation, a plastic pod of solvent for AgX (usually $Na_2S_2O_3$), and a printing layer. All three are enclosed in a lightproof paper envelope arranged so that the negative layer can be pulled out into the camera. After exposure, it is returned to the envelope where a roller breaks the pod and, by a squeegee action, coats the negative with solvent. The thiosulfate diffuses into the negative layer and, where no light struck, dissolves the silver halide grains as a complex. The complex diffuses into the printing layer which contains a catalyst and nuclei not sensitive to light. The silver-containing complex is reduced, giving directly a positive image.

The color film is even more interesting because it is more complex and involves more complicated chemicals. The film consists of 14 layers which occupy only 0.002"—not much more than the thickness of a human hair.

The final picture is made of three primary colors, each of which requires three layers in the film. The remaining layers contain the print paper, a coating polymer, a pod of activator chemicals, and an image-receiving layer. We can understand the general method by seeing how the green part of the picture is formed.

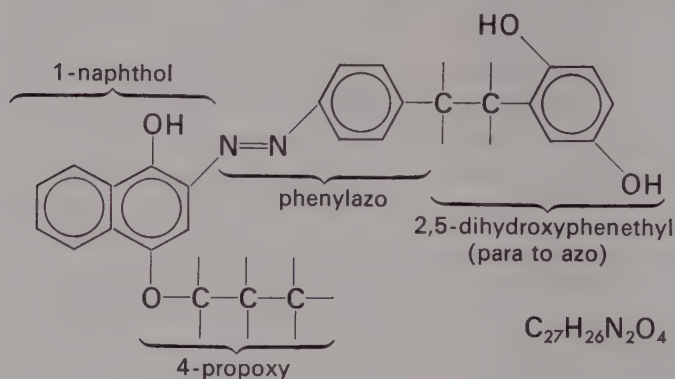
There is one layer in the film containing silver

halide grains sensitive to green light. Next to it is a layer containing a chemical that is both a developer and a magenta dye. The third layer is a spacer. When the green light from the subject strikes the AgX grains, *some* of them are activated. To start development a roller breaks the pod of activator and these chemicals diffuse through the film releasing the developer dye. The exposed AgX grains immobilize the red dye molecules but allow the yellow and blue dye molecules from other layers to pass. The various

combinations of dyes reaching the image layer produce different colors and shades. All these reactions are carefully controlled by the concentration of reagents and the diffusion times required. About 50 seconds are needed. Finally the image layer is polymerized to a clear, glassy, neutral material which is resistant to scratches.

An example of the complexity of the developer-dye molecules is seen in the following compound; one of those for the magenta layer. It is

2[p-(2,5-dihydroxyphenethyl)phenylazo]-4-propoxy-1-naphthol.



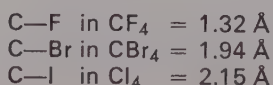
Note the presence of a hydroquinone-like portion at the right end of the molecule. This is the

developer portion. The azo part to the left is the dye.

Answers to Exercises and Problems

Exercise 19-1

Use the carbon atom covalent radius 0.77 Å and the covalent radii given in Figure 19-2 to predict C—X bond length in each of the following molecules: CF_4 , CBr_4 , Cl_4 . Compare your values with the experimental ones:



Answer

	Calculation	Observed
CF_4	0.77	
	0.72	
	1.49 Å	1.32 Å
CBr_4	0.77	
	1.14	
	1.91 Å	1.94 Å

Cl_4	0.77	
	1.33	
	2.10 Å	2.15 Å

Problem 1

Give the electron configuration for each of the trio F^- , Ne , Na^+ . How do the trios Cl^- , Ar , K^+ , and Br^- , Kr , Rb^+ differ from the above?

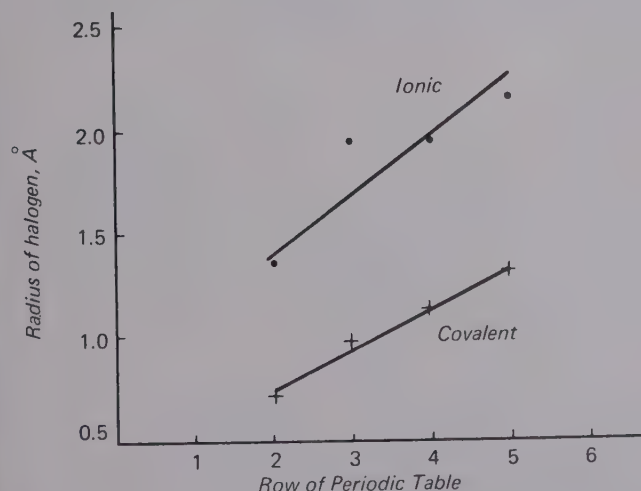
Answer

F^-	$1s^2 2s^2 2p^6$
Ne	$1s^2 2s^2 2p^6$
Na^+	$1s^2 2s^2 2p^6$

Each of these species has the *same* electron configuration. They are called isoelectronic. The species Cl^- , Ar , K^+ all have more electrons $1s^2$, $2s^2 2p^6$, $3s^2 3p^6$, and Br^- , Kr , Rb^+ have still more: $1s^2$, $2s^2 2p^6$, $3s^2 3p^6$, $3d^{10} 4s^2 4p^6$. The second trio is larger than the first by the $3s^2 3p^6$ electrons; the third is larger than the second by the $3d^{10} 4s^2 4p^6$ electrons. Note that, in each trio, the outermost groups are the same kind of electrons, $s^2 p^6$.

Problem 2

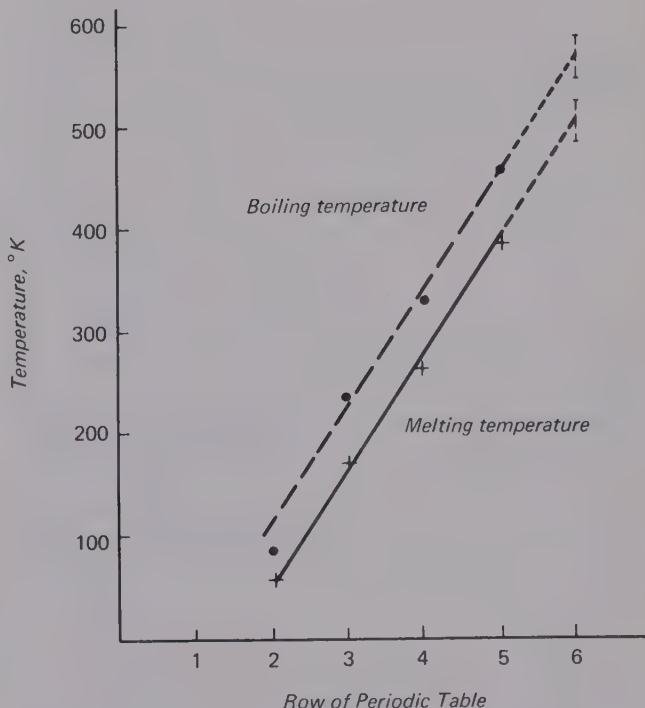
Table 19-1 contains values for the covalent radii and the ionic radii of the halogens. Plot both radii versus row number. What systematic changes are evident in the two curves?

Answer

In both curves the increase in radius is almost linearly related to row number. In both cases the change from fluorine to chlorine is sharper than the subsequent changes from chlorine to bromine to iodine. Remember that fluorine and chlorine are not as widely separated in atomic number as are chlorine, bromine, and iodine. Successive electron levels do not add as much to radius, because the increased nuclear charge pulls the inner levels in.

Problem 3

Using the data from Table 19-1, plot on one set of axes the melting and boiling temperatures of the halogens versus row number.

Answer

The curves are nearly linear with row number. Recall that in Chapter 6 the student learned that the physical properties of all columns do not change in the same way (the alkali metals have the opposite trend in melting temperature). Avoid the incorrect idea that melting temperature always increases as molar mass increases.

Problem 4

For astatine, use your graphs from Problems 2 and 3 as a basis for a prediction of its covalent radius, ionic radius of the At^- ion, melting and boiling temperatures.

Answer

If we use the graphs from Problems 2 and 3, we see that the covalent radius would probably be in the range 1.4–1.6 Å. The ionic radius would be expected to be 2.2–2.5 Å. The melting temperature would be expected to be 480–530°K (207–257°C). The boiling temperature would be expected to be 550–600°K (277–327°C).

For the radii, the span of atomic number from iodine to astatine is 32, as contrasted with 18

from bromine to iodine. This might explain why the astatine radii may be somewhat higher than a linear extrapolation would make it. Note that a similar question was asked in Problem 6, Chapter 7.

Problem 5

Predict the molecular structures and bond lengths for SiF_4 , SiCl_4 , SiBr_4 , and SiI_4 , assuming the covalent radius of silicon is 1.16 Å.

Answer

The bonding in silicon is that described as sp^3 , and the bonds are tetrahedrally oriented, as in CF_4 , shown in Textbook Figure 17-4. The predicted bond lengths are:

	Si—F	Si—Cl	Si—Br	Si—I
Silicon radius	1.16 Å	1.16 Å	1.16 Å	1.16 Å
Halogen radius	+ .72	+ .99	+ 1.11	+ 1.33
Calculated bond length	1.88 Å	2.15 Å	2.27 Å	2.49 Å
Experimental bond length	(1.59 Å)	(2.01 Å)	(2.15 Å)	(2.43 Å)
Difference	0.29 Å	0.14 Å	0.12 Å	0.06 Å

Notice the trend in the difference between predicted and experimental values. This trend can be explained in terms of the *difference* in ionization energies. The very large difference between E_1 of silicon and E_1 of fluorine implies ionic character in the bond, which tends to strengthen and shorten the bond. This ionization energy difference decreases from 224 kcal, F—Si, to 53 kcal, I—Si.

Problem 6

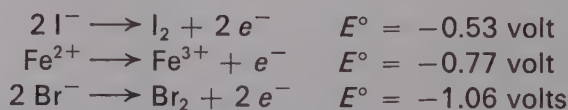
Explain in terms of nuclear charge why the K^+ ion is smaller than the Cl^- ion, though they are isoelectronic (they have the same number of electrons).

Answer

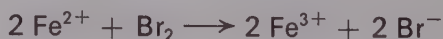
These two ions have the same number of electrons, in the same orbitals, but the greater nuclear charge in K^+ "pulls" the electrons closer to the nucleus, and it is smaller than that of Cl^- . The values of ionic radii are: K^+ , 1.55 Å; Cl^- , 1.81 Å.

Problem 7

Can aqueous bromine, Br_2 , be used to oxidize ferrous ion, Fe^{2+} , to ferric ion, Fe^{3+} (use Appendix 4)? Can aqueous iodine, I_2 , be used instead of bromine?

Answer

Since Fe^{2+} is above Br_2 in the E° table, Fe^{2+} is the more readily oxidized substance. Products are favored at equilibrium.

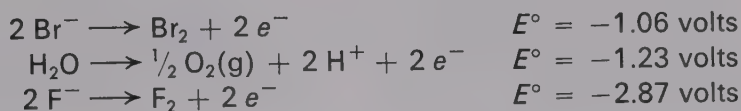


Since Fe^{2+} is below I_2 in the E° table, I_2 is the more readily oxidized substance, and the reaction will not occur appreciably. (In fact, the reverse reaction furnishes a practical means of reducing Fe^{3+} to Fe^{2+} .)

Problem 8

What will happen if F_2 is bubbled into 1 M $NaBr$ solution? Justify your answer using E° values.

Answer



By the E° values, fluorine can oxidize either Br^- or H_2O , producing Br_2 and O_2 . Both of these reactions would be expected to occur, but

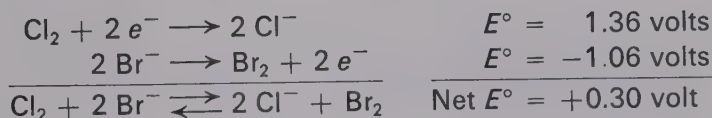
the relative amounts would depend upon the conditions.

Problem 9

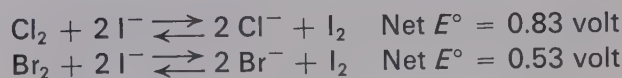
Use E° values to predict what will happen if chlorine is added to a 1 M solutions of Br^- , of I^- . What will happen

if Br_2 is added to 1 M I^- ? Which halogen is oxidized and which is reduced in each case?

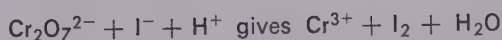
Answer



Cl_2 will be reduced to $2 Cl^-$, thus oxidizing $2 Br^-$ to Br_2 . Bromine will be formed. Similar equations will hold for each pair tested:

**Problem 10**

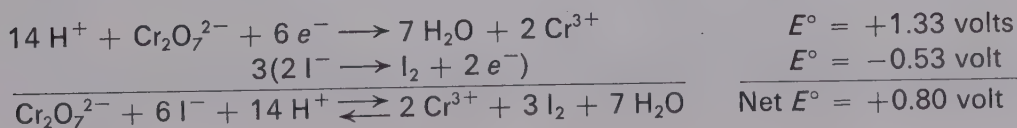
Write a balanced equation for the reaction of dichromate and iodide ions in acid solution. Determine E° for the reaction



Answer. $E^\circ = +0.80$ volt.

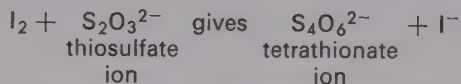
Answer

Using the E° table of half-reactions, we find



Problem 11

Balance the equation for the reaction of iodine with thiosulfate ion:



Answer

The equation can be balanced by inspection



The oxidation number of sulfur in $\text{S}_4\text{O}_6^{2-}$ is

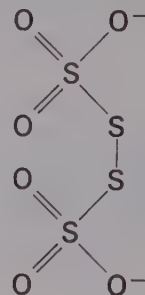
$$4(\text{oxid. no. S}) + 6(-2) = -2$$

$$\text{oxid. no. S} = \frac{-2 + 12}{4} = \frac{10}{4} = 2.5$$

The fractional oxidation number can be taken as a clue that not all the sulfur atoms in tetrathio-

What is the oxidation number of sulfur in the tetrathionate ion?

nate are identical. The ion is thought to have the structure



which does have two kinds of sulfur atoms.

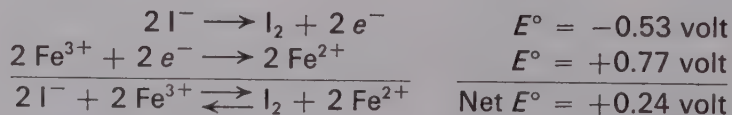
Problem 12

How many grams of iodine can be formed from 20.0 grams

of KI by oxidizing it with ferric chloride (FeCl_3)? Determine E° .

Answer. 15.3 grams of I_2 .

Answer



$$\text{moles} = \frac{\text{grams}}{\text{grams/mole}} \quad 20.0 \times \frac{1}{166} = 0.120 \text{ mole KI}$$

$$(\text{moles KI}) \left(\frac{\text{moles I}_2}{\text{mole KI}} \right) \quad 0.120 \times \frac{1}{2} = 0.0600 \text{ mole I}_2$$

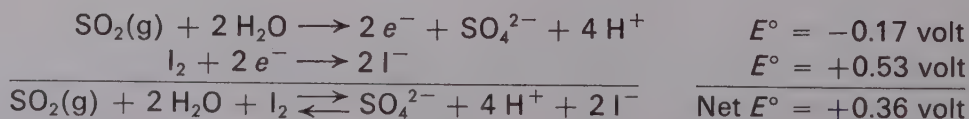
$$(\text{moles I}_2) \left(\frac{\text{g}}{\text{mole}} \right) \quad 0.0600 \times 254 = 15.3 \text{ g I}_2$$

Problem 13

Balance the equation for the reaction between SO_2 and I_2 to produce SO_4^{2-} and I^- in acid solution. Calculate E° .

From Le Chatelier's Principle, predict the effect on the E° in this reaction if $\text{H}^+ = 10^{-7} M$ is used instead of $\text{H}^+ = 1 M$.

Answer

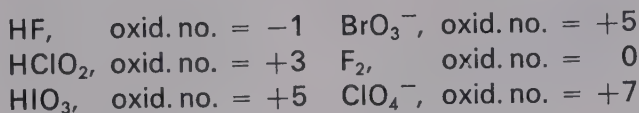


By Le Chatelier's Principle, reducing the concentration of a product increases the tendency to

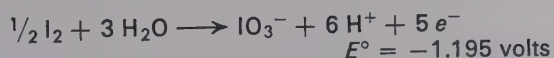
form products. Hence Net E will be still more positive in dilute H^+ .

Problem 14

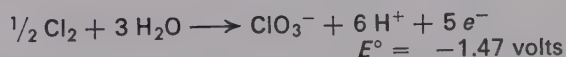
What is the oxidation number of the halogen in each of the following: HF, HClO₂, HIO₃, BrO₃⁻, F₂, ClO₄⁻?

Answer**Problem 15**

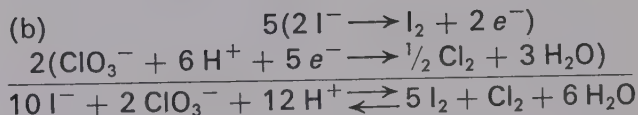
Comparable half-reactions for iodine and chlorine are shown below.

**Answer**

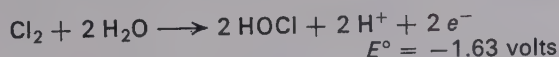
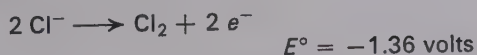
- (a) Chlorate ion is a stronger oxidizing agent than iodate ion because the E° for Cl₂, ClO₃⁻ is more negative than that for I₂, IO₃⁻.



- (a) Which is the stronger oxidizing agent, iodate, IO₃⁻, or chlorate, ClO₃⁻?
- (b) Balance the equation for the reaction between chlorate ion and I⁻ to produce I₂ and Cl₂.

**Problem 16**

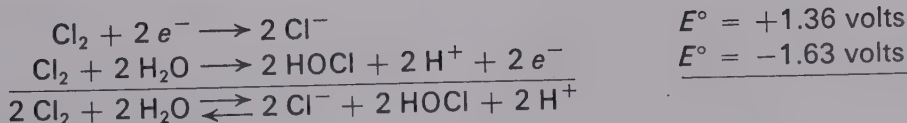
Two half-reactions involving chlorine are



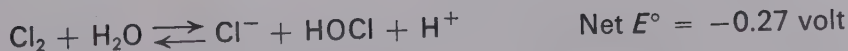
- (a) Balance the reaction in which self-oxidation-reduction of Cl₂ occurs to produce chloride ion and hypochlorous acid, HOCl.
- (b) What is the oxidation number of chlorine in each species containing chlorine?
- (c) What is E° for the reaction?
- (d) Explain, using Le Chatelier's Principle, why the self-oxidation-reduction reaction occurs in 1 M OH⁻ solution instead of 1 M H⁺.

Answer

- (a) Reversing the first reaction, we have



or



- (b) Cl₂ (oxid. no. = 0); Cl⁻ (oxid. no. = -1); HOCl (oxid. no. = +1).
- (c) $E^\circ = -0.27 \text{ volt}$.
- (d) Changing the concentration of H⁺ from 1 M

to 10⁻¹⁴ M (as it is in 1 M OH⁻) increases the tendency to form products so as to partially compensate for the removal of H⁺. Equilibrium is shifted to favor products.

Problem 17

From each of the following sets, select the substance which best fits the requirement specified.

- | | |
|--------------------------------|---|
| (a) Strongest acid | HOCl, HOClO,
HOClO ₂ |
| (b) Biggest atom | F, Cl, Br, I |
| (c) Smallest ionization energy | F, Cl, Br, I |
| (d) Best reducing agent | F ⁻ , Cl ⁻ , Br ⁻ , I ⁻ |
| (e) Weakest acid | HF, HCl, HBr, HI |
| (f) Strongest hydrogen bonding | HF, HCl, HBr, HI |

Answer

- (a) HClO₃ (HOClO₂); explained in Section 19-4.
 (b) I; explained in Section 19-2.
 (c) I; explained in Section 19-1.
 (d) I⁻; explained in Section 19-3.
 (e) HF; explained in Appendix 3 of Textbook.
 (f) HF; explained in Chapter 10 of Textbook.

Part (f) may be hard for the student. The better students may get the correct answer by comparing Textbook Figure 10-6, page 186.

Problem 18

Describe two properties that the halogens have in common and give an explanation of why they have these properties in common.

Answer

- (a) They exist as diatomic molecules in the gas phase. This is explained by noting that each atom has one unshared electron. Two atoms can share these unpaired electrons, thereby forming a covalent bond. This sharing fills all the valence orbitals without using a higher energy level, hence the molecules are diatomic, not triatomic, etc.
 (b) All halogens form compounds of the form MX, where M is an alkali metal and X is a halogen. The reason for this is that each alkali atom can donate one electron (leaving a noble gas electron configuration), whereas each halogen can accept an electron, thereby also gaining the electron configuration of a noble gas. Hence one atom of an alkali satisfies one atom of a halogen.
 (c) All halogens form covalent bonds with hydrogen and with carbon. The reason for this is, again, the possibility of sharing electrons without using orbitals of greater

energy than are used by the electrons of the atom.

- (d) All halogens form compounds with the alkali metals (and others), which form ionic solids. The reason is that given in (b); in addition, the electron configuration of the noble gas has spherical symmetry. This allows the formation of undirected (i.e., ionic) bonds.
 (e) All the halogens have some oxidizing ability. This is a result of their affinity for electrons.
 (f) All the halogens can be made gaseous at fairly low temperatures. This is a result of their molecular (rather than ionic or network) structures. Their limited capacity to form bonds leads to their simple structure.

Problem 19

How many grams of SiO₂ would react with 5.00×10^2 ml of 1.00 M HF to produce SiF₄?

Answer

$$\left(\frac{\text{ml}}{\text{ml/liter}} \right) \left(\frac{\text{moles}}{\text{liter}} \right)$$

$$\left(\frac{5.00 \times 10^2}{1000/1} \right) (1.00) = 0.500 \text{ mole HF}$$

$$(\text{moles HF}) \left(\frac{\text{moles SiO}_2}{\text{mole HF}} \right)$$

$$0.500 \times \frac{1}{4} = 0.125 \text{ mole SiO}_2$$

$$(\text{moles SiO}_2) \left(\frac{\text{g}}{\text{mole}} \right)$$

$$0.125 \times 60.1 = 7.51 \text{ g SiO}_2$$

Problem 20

A water solution that contains 0.10 M HF is 8% dissociated. What is the value of K_A ?

Answer. 6.9×10^{-4} .

Answer

$$K_A = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{(0.008)^2}{(0.10 - 0.008)} \\ = \frac{64 \times 10^{-6}}{9.2 \times 10^{-2}} = 6.9 \times 10^{-4}$$

This problem was also given as 27 in Chapter 14.

The Fourth-Row Transition Elements



Intent and Approach

Approach this chapter as new material with respect to description and as old material with respect to chemical principles. Although the elements studied are new, the chapter can be a valuable review of chemical principles. Emphasize the principles as much as possible; avoid letting the descriptive material hide them.

The first portion of this chapter applies previously learned principles of electron configuration to *d* orbitals. Complex ions are treated much more extensively than before, building on previously developed concepts of molecular shape and its relations to electron configuration. The

rest of the chapter, dealing with specific properties of the transition elements, offers an opportunity to stress regularities.

The chapter is intended to show the student:

- (1) the regularities shown by elements with *d*-orbital valence electrons;
- (2) the nature of complex ions and complex compounds;
- (3) the relation between certain specific properties of transition elements and some of the chemical theories he has already learned.

Outline

The transition elements are defined and their electron configurations examined (20-1). Common properties are discussed in Section 20-2.

Some of the variety in oxidation number and types of compounds formed is explored for chromium as an example (20-3).

Complex ions and their geometry are treated (20-4, 20-5).

Natural complexes get brief mention (20-6).

The most commonly used transition element is iron. Section 20-7 contains some discussion of its production and uses.

New Concepts

This chapter is to show the use of concepts learned earlier.

SCHEDULE AND RELATED MATERIAL

Suggested Time : 7 days

Text Section	Topic and Other Work	Exercises	Problems		
			Easy	Medium	Hard
20-1	Electron Configurations	1, 2	1	2, 3	
20-2	Some Properties and Regularities	3		8, 10	
20-3	Some Compounds of Chromium			9	
20-4	Complex Ions			16	
20-5	The Geometry of Complex Ions		4	5-7	11
20-6	Expt. 43, Anion Exchange Complexes Found in Nature				
20-7	Expt. 44, Preparation of a Complex Salt Iron, Workhorse of the Metals <i>Film:</i> Vanadium, A Transition Element		12, 17	13-15	

Expts. 45 and 46 are optional ; see p. 416.

Development

Present this chapter first as an extension of previous knowledge and second as descriptive chemistry.

Of the concepts studied earlier, the more important (to this chapter) are :

Electron configuration	Isomerism
Ionization energy	Equilibrium
Geometry of molecules	Acid-base theory

Less important (to this chapter) are :

Oxidation-reduction
Reaction rates
Energy in reactions

elements. The number of valence electrons is fixed by the energy needed to remove them, and the buried *d* electrons have little effect on this.

20-2 Some Properties and Regularities of the Fourth-Row Transition Elements

Show that the trends given follow those already learned *when* the "buried" position of *d* electrons is known. Problem 8 and Exercise 20-3 help show such trends.

20-3 Some Compounds of Chromium

This section gives some idea of the variety of compounds formed by transition elements. Table 20-3 shows the same point for oxides. Draw attention to the common occurrence of +2 and +3 oxidation numbers. Relate them to the total number of valence electrons for the elements Sc through Cr or Mn and the *unpaired* valence electrons for the latter half of the row. One or two electrons can be promoted to the 4*p* level but usually no more.

20-1 Electron Configurations

The orbital diagram, Textbook Figure 20-1, will help make the use of 3*d* orbitals reasonable. Exercises 20-1 and 20-2 will help review the electronic structure. The *d* orbitals are somewhat buried, with the result that electrons in them are not readily accessible. This means they do not occupy "new" space at the outer part of the atom. This helps account for the near constancy of the atomic radius found for transition

20-4 Complex Ions

You will note that on Textbook p. 401, and later in the chapter, some compounds are given without names. This omission is deliberate, and is to avoid opening the door to a long discussion of inorganic nomenclature. Names for the compounds are:

- $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$;
 hexaamminechromium(III) trichloride
 $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$;
 chloropentaamminechromium(III) dichloride
 $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$;
 dichlorotetraamminechromium(III) chloride
 $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$;
 trichlorotriamminechromium(III)
 K_3CrF_6 ;
 potassium hexafluorochromate(III)
 $\text{Na}_3\text{Cr}(\text{CN})_6$;
 sodium hexacyanochromate(III)
 $\text{KCr}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$;
 potassium chromium sulfate dodecahydrate,
 "chrome alum"

Naming such compounds will probably be interesting to only a few students; hence it is preferable that the class, as a whole, concentrate on the other aspects of complex ions.

20-5 The Geometry of Complex Ions

In approaching this section a brief review of solid geometrical figures may be useful. In particular the octahedron and tetrahedron should be demonstrated: the octahedron has eight triangular faces; the tetrahedron has four triangular faces. Note, however, that there are six (*not* eight) corners on the octahedron, and four on the tetrahedron. Link these shapes to coordination numbers (recall Expt. 38) and to the shapes of d^2sp^3 and sp^3 orbital representations (see the *Background Discussion* for the shape of d orbitals). The CrCl_3 -ammonia complexes on Textbook p. 402 can best be illustrated with models and by referring to Figure 20-3 in the Textbook. The compound $\text{Cr}(\text{NH}_3)_6\text{Cl}_3$ has the structure in which the three Cl^- ions are rather loosely attached. Here we have a complex cation. As

fewer NH_3 molecules are involved, chloride ions join the complex structure and are more firmly held. These firmly held chloride ions do not precipitate with Ag^+ .

The discussion of ion geometry begins with coordination number—the number of *near* neighbors. The groups bound to a central atom do not necessarily lie at the same distance from it. This effect is observed for so simple a molecule as Al_2Cl_6 and is explained as resulting from different electronic environment—hence different bonding distances. In Al_2Cl_6 each Al is surrounded by four near chlorine atoms in a tetrahedral arrangement. The outer four chlorine atoms are 2.06 Å from the Al; the center two are 2.21 Å from the Al. The coordination number of Al is 4.

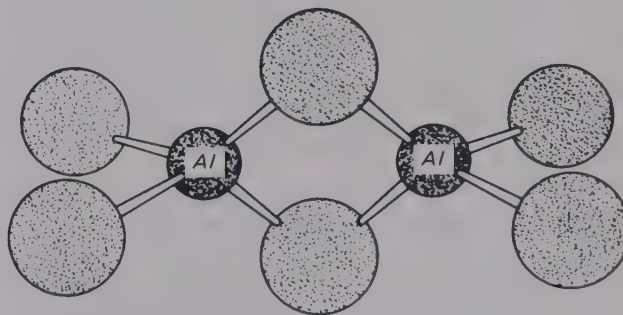


FIGURE 20-1

Structure of Al_2Cl_6 .

As another example, dichromate ion can be considered as two tetrahedra joined at one corner (see Textbook Figure 20-2, p. 400). The outer O—Cr distance is 1.63 Å, the O—Cr distance in the Cr—O—Cr bonds is 1.91 Å.

A portion of the background material discusses models of some simple complexes. The bond distances are given with angles, as needed. The arrangements will be most clear if a ball-and-stick model is made so that the central ion can be seen. If this is done, be sure to stress that the sticks do not represent bonds.

The principal shapes of complexes are linear (sp bonding), square planar (dsp^2), tetrahedral (sp^3), and octahedral (d^2sp^3). Only the second and last are new. Illustrate these shapes with the models described in the *Background Discussion*.

Be sure to point out that bonding in complexes is not different from the kind that the student has already studied. Stable arrangements exist because electrons find energetically favorable positions between two nuclei. As in simpler molecules and ions, the extremes in type are called ionic and covalent bonds. In actual complex ions we find not only these types but intermediate ones of partial ionic character. The entire situation is no different from that described in Chapter 10. The presence of d orbitals gives no new bonding types, only some new shapes, as described above.

**Expt. 43, THE SEPARATION OF IRON,
COBALT, AND NICKEL IONS WITH
AN ANION EXCHANGE RESIN,**

fits here. See p. 245 in the Laboratory Guide.

20-6 Complexes Found in Nature

Many reactions in plant and animal chemistry involve complex ions, but the examples given are probably enough for the student at this stage. The CO poisoning example on p. 404 of the Textbook provides a good opportunity to review equilibrium principles.

**Expt. 44, PREPARATION OF A COMPLEX
SALT,**

fits here. See p. 249 in the Laboratory Guide.

20-7 Iron, Workhorse of the Metals

This section deals with such an important metal that it is worth more effort than the others. You should use the preparation of iron as an example

of a common method of freeing metals from their oxide ores. The first step is chemical reduction, giving the metal, which is then purified of reducing agent and any unwanted "slag" that formed. Finally, the pure form is made impure in a controlled way to produce desired properties—it is alloyed.

**Film, VANADIUM, A TRANSITION
ELEMENT,**

fits here. See p. 418 for summary.

Properties of Fifth- and Sixth-Row Transition Elements

Tables 20-1 and 20-2 give some selected data for the transition elements in the fifth and sixth rows of the Periodic Table, and provide a chance for you to test the student's skill; correlations between members of a column can be readily noted.

An orbital diagram can be used to relate the trends in ionization energy and atomic radius to electronic configuration. The "contraction" of atomic radius results from the action of an increasing number of protons on the electrons in orbitals of fixed size (more or less). Ionic radii show the same trend but to a reduced extent.

Optional Experiments

The following experiments can be used for student projects or class laboratory work as desired.

Experiment 45: Preparation of Potassium Dichromate

Experiment 46: Preparation of Chrome Alum

They are not integral parts of the chapter but do apply to the material covered. See pp. 252 and 255 in the Laboratory Guide.

Experiment 35: Corrosion of Iron is related to Section 20-7. If it was not done in Chapter 15, it could fit in this chapter.

TABLE 20-1
Some Properties of the Fifth-Row Transition Elements

Element	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Atomic number	39	40	41	42	43	44	45	46	47	48
Atomic radius* (Å)	1.80	1.57	1.47	1.40	1.36	1.33	1.34	1.37	1.44	1.48
Ionization energy (kcal/mole)	149	159	—	169	—	177	177	191	173	206
Density (g/cm ³)	4.34	6.54	8.58	10.2	11.50	12.30	12.42	12.03	10.50	8.64
m.t. (°C)	1500	2100	1950	2600	2140	2400	1966	1555	960	324
b.t. (°C)	—	3600	5100	4800	—	4200	3900	3170	1980	767
Ionic radius of M ⁴⁺ (Å)	1.06(3+)	0.87	0.69	0.68	—	0.63	0.68(3+)	—	1.13(1+)	1.03(2+)
E° (volts) M → M ²⁺ + 2 e ⁻	—	—	~1.1(3+)	~0.2(3+)	—	—	~-0.8(3+)	-0.987**	-1.389	+0.40

Note: The E° values (in acid solution) are from W. M. Latimer, *Oxidation Potentials*, Prentice-Hall, Englewood Cliffs, N. J. (1952).
* For coordination number 12 (a few are corrected to this condition).
** 4 M HClO₄.

TABLE 20-2
Some Properties of the Sixth-Row Transition Elements

Element	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Atomic number	57	72	73	74	75	76	77	78	79	80
Atomic radius (Å)	1.86	1.57	1.47	1.40	1.38	1.35	1.35	1.37	1.44	1.60
Ionization energy (kcal/mole)	129	—	—	186	—	200	207	204	211	238
Density (g/cm ³)	6.18	13.31	16.69	19.1	20.9	22.7	22.65	21.45	19.3	13.5
m.t. (°C)	826	2300	3010	3400	3150	2700	2454	1774	1063	-39
b.t. (°C)	—	5200	6000	5700	—	4600	4500	3800	2700	357
Ionic radius of M ⁴⁺ (Å)	1.04(3+)	0.84	0.68(5+)	0.68	—	0.63	0.63	—	—	1.12(2+)
E° (volts) M → M ²⁺ + 2 e ⁻	2.52(3+)	—	—	0.11(3+)	~-0.3	~-0.85	<-1.1	~-1.2	-1.50(3+)	-0.79

Note: The E° values (in acid solution) are from W. M. Latimer, *Oxidation Potentials*, Prentice-Hall, Englewood Cliffs, N. J. (1952).

Supplementary Material

Book

F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience Publishers, 1966, N. Y. A good source for the teacher. The sections on orbitals and ligand field theory give a nonmathematical treatment.

Film

For ordering information see the *List of Film Sources* at the back of the Teacher's Guide.

VANADIUM, A TRANSITION ELEMENT

A CHEM Study film

Running Time: 22 minutes

The collaborator, Professor Robert Brasted, University of Minnesota, shows vanadium as a typical transition element. The different oxidation states and their colors are identified via titration with cerium solution. The oxidation states and the observed colors are correlated with the electronic structures using an orbital diagram. The formation of complex ions containing vanadium in various oxidation states is demonstrated. The variations in properties are discussed in terms of ion size and charge density.

Background Discussion

The discussion of this chapter is presented in five sections. The order is:

- Complexes—Definition and Detection
- d* Orbitals
- Models of Complex Ions
- Ion Exchange
- Amphoteric Complexes

Complexes—Definition and Detection

For most purposes it is sufficient to define a complex ion as *an ion containing a central atom* to which others are joined*. Most commonly, the central atom is from a metallic element. If this definition is mentioned after Section 20-5 (on geometry), then the meaning of "in the center" will be clear. Do not attempt to make a rigid definition, because there is no universally accepted one. Common occurrence and usage have taken sulfate, nitrate, and a few other ions out of the complex class, although they could well be included.

* Remember, an atom can be either charged or neutral. Using this convention, one can refer to the Mn *atom* in KMnO_4 without specifying whether it is neutral or charged.

Following the identification of complex ions, special forces were invented to explain them. The then current bonding theories could not account for them. Additional structural information and advances in bond theory have erased this need. Bonds in complexes are explained by the same kind of orbital overlap and electron pairing that has been used in this course for simpler compounds (Chapter 10).

Complexes can be detected in a number of ways, although the convincing proof is much harder to give. The following list touches briefly on some methods.

- | | |
|----------------------|---|
| X-ray
Diffraction | For solids this is the most convincing test. It is complicated and tells nothing about what exists in solution. But it does give quite specific information about structure. It is the source of the dimensions for models such as those discussed on p. 420. |
| Ion Integrity | Complex ions have "integrity" in reactions, just as organic groups have skeletal integrity. |

Colligative Properties Conductivity, osmotic pressure, freezing temperature, etc. can provide evidence of the number of particles obtained from a unit.

Electrolysis If an element which normally forms a positive ion is concentrated around the positive (instead of negative) electrode, one possibility is that it is part of a complex anion.

Color Change The usual example is white CuSO_4 , which turns blue when water is added. The water-copper complex gives the color. This method is a useful, although rough, guide once other, more positive proof has been provided for the presence of a complex.

d Orbitals

The bonding exhibited by transition elements requires the use of *d* orbitals. Like *s* and *p* orbitals, these represent volumes in which electrons are most likely to occur. A bond can be represented by an overlap of two orbitals (as in Chapter 16). This overlap produces a region of high electron density, and consequently, a region to which nuclei are attracted.

We commonly represent *d* orbitals as shown in the five diagrams of Figure 20-2.

Note: Each diagram shows *one d orbital*, which has a capacity of only two electrons. Some of the diagrams can be confused as showing two *p* orbitals, especially the $d_{x^2-y^2}$ orbital. Refer to the papers by DeVault (mentioned on p. 153) and to Figure 9-3 (p. 151) for information about the energy of 3*d* orbitals and how the energy changes with atomic number.

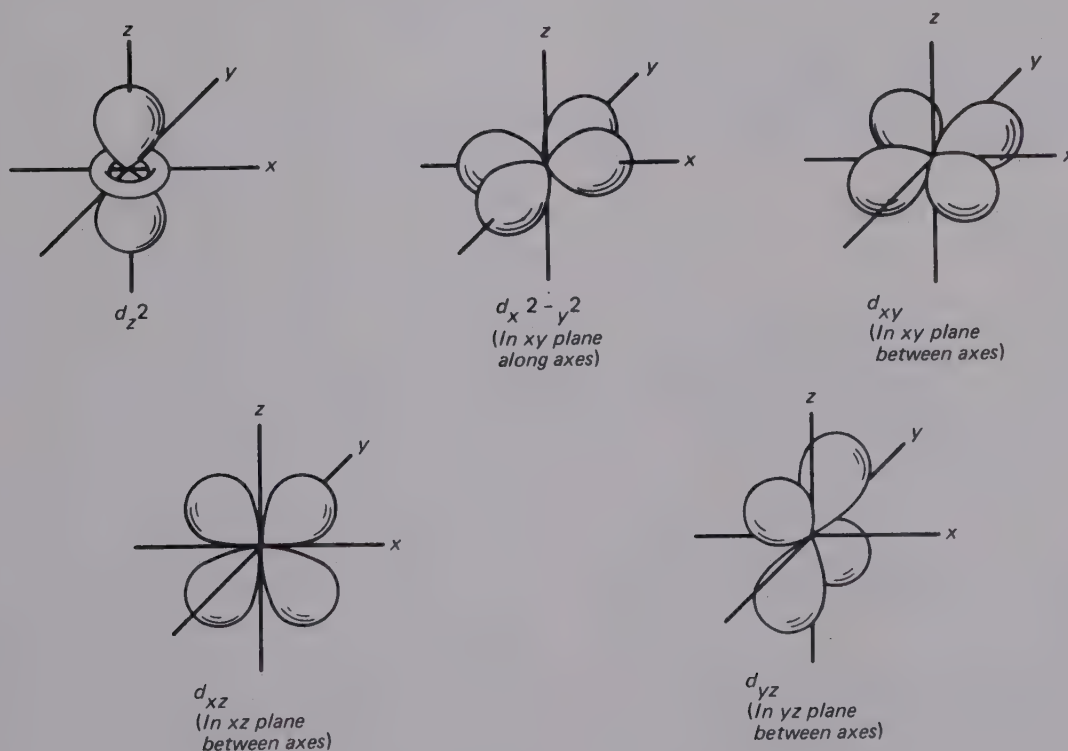


FIGURE 20-2

Schematic diagrams of *d* orbitals.

Models of Complex Ions

Some students may express interest in the size and appearance of these complex substances. A good source of information, from which the following examples are taken, is *Interatomic Distances*, and the supplement edited by L. E. Sutton, The Chemical Society, London (1958). Others are A. F. Wells, *Structural Inorganic Chemistry*, Oxford, at the Clarendon Press (1962), and L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press (1960). The atomic radii are from Pauling.

I. $(\text{AlF}_6)^{3-}$ (octahedral)

Al—F distance = 1.81 Å

Occurs in Na_3AlF_6 [trisodium hexafluoroaluminate(III)]

Radii: $\text{Al}^{3+} = 0.50$; $\text{F}^- = 1.36$ Å

II. $(\text{VO}_4)^{3-}$ (tetrahedral)

V—O = 1.86 Å

Occurs in BiVO_4 (bismuth vanadate)

Radii: $\text{V}^{5+} = 0.59$; O = 1.40 Å

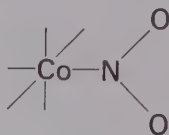
III. $[\text{Co}(\text{NO}_2)_6]^{3-}$ (octahedral)

Occurs in $\text{K}_3\text{Co}(\text{NO}_2)_6$ [tripotassium hexanitrocobaltate(III)]; referred to in questions as cobaltinitrite

Co—N = 2.03 Å

N—O = 1.1

O...O = 2.1



Radii: $\text{Co}^{3+} \sim 0.7$; N = 0.74; O = 1.40 Å

IV. $\text{Ni}(\text{CN})_4^{2-}$ (square planar)

[tetracyanonickelate(IV) ion]

Ni—C = 1.95 Å; C—N = 1.30 Å

Radii: $\text{Ni}^{4+} \sim 0.5$; C = 0.77; N = 0.74 Å

V. $\text{PtBr}_4(\text{NH}_3)_2$ (octahedral)

[tetrabromodiammineplatinum(IV)]

Pt—N = 2.01 Å

Pt—Br = 2.44

N—H = 1.01 ($\angle \text{H—N—H} = 107^\circ$)

Radii: $\text{Pt}^{4+} = 1$ (est.); $\text{Br}^- = 1.85$;

N = 0.74; H = 0.34

VI. $[\text{Pd}(\text{NO}_2)_4]^{2-}$ (square planar)

[tetranitropalladate(II) ion]

Pd—N = 2.10 Å ($\angle \text{N—Pd—N} = 90^\circ$;

$\angle \text{Pd—N—O} = 112^\circ$)

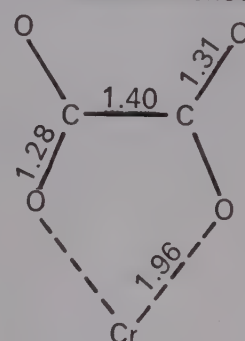
N—O = 1.14 ($\angle \text{O—N—O} = 136^\circ$)

Radii: $\text{Pd}^{2+} = 0.86$; N = 0.74; O = 1.40 Å

VII. $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ (octahedral)

[tris(oxalato)chromate(III) ion]

The oxalate group is planar, and has the dimensions shown.



Radii

Cr^{3+}	0.65 Å
C	0.77
O	1.40

This complex illustrates a "bidentate" (two-tooth) complexing group. Organic molecules with three, four, and six complexing groups are known.

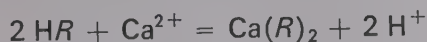
Ion Exchange

Ion exchange is a process of considerable commercial value. Its name is self-explanatory. Ions from a solution are exchanged (adsorbed) for other ions from the exchange medium. This medium is most commonly a solid polymer containing polar groups which act as exchange sites.

Some exchange polymers (resins) are organic—either natural ones (cellulose, polyamides from silk, or carbonaceous matter from coal), which have been treated to give (or increase) ion adsorption, or synthetic polymers made from monomers containing the desired groups. Some exchangers are inorganic—usually silicate or aluminate minerals. Clays and zeolites are the best examples.

The polymer can be regarded as a huge ion of one type (cation or anion) with many small, soluble ions of the other type on its surface. The classifications *anionic resin* and *cationic resin* are determined by the nature of the small, soluble ion. Anionic resins exchange anions. This exchange is an equilibrium process—one that is subject to the equilibrium principles described in Chapter 13. The regeneration of resins involves

changing the environment so as to favor one equilibrium state over another. To illustrate this, let us consider the cationic resin HR where R is a site on the resin which releases a proton. The exchange of Ca^{2+} is then written



With a "good" resin, the removal of Ca^{2+} will be essentially complete, and the equilibrium constant for the above reaction will be large. But by increasing H^+ ion concentration (by "back-washing" with acid), the reaction is reversed, the original state of the exchanger is restored, and the Ca^{2+} is discarded in the wash solution.

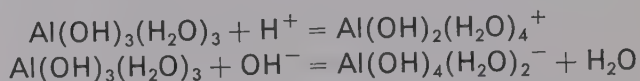
The main use of ion exchange resins is in the treatment of water. On a commercial scale, water softening (exchanging Na^+ for Ca^{2+} and Mg^{2+}) is the major example. In the laboratory, it is more usual to find mixed resins used to demineralize water. In this case all cations are replaced by H^+ , and all anions by OH^- , so that the result is extremely pure water. The purification of seawater by this technique is possible, but it is still prohibitively expensive.

Other uses include the purification of many products—sugar, milk, beer, and pharmaceutical products. The commercial separation of rare

earths (similar to Expt. 43 on Fe, Co, and Ni) is made practical by ion exchange resins.

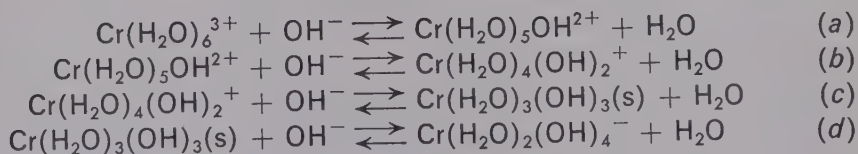
Amphoteric Complexes

Amphoteric (from the Greek word for "both") means that a compound can function as an acid or a base. It is most commonly applied to hydroxides, and indicates that they react to give a new species in either acidic or basic solutions. The behavior is not unique with complex ions or with transition elements. Note the equilibria



These are only the first steps; the process can be continued until the final ions are $Al(H_2O)_3^{3+}$ and $Al(OH)_6^{3-}$, respectively. Compounds exist for each stage, for instance, $Ca_3[Al(OH)_6]_2$, tricalcium hexahydroxyaluminate(III).

As another example, consider the following equations which summarize the steps believed to occur when $NaOH$ is slowly added to a solution of chromic ion. Step (c) corresponds to formation of solid hydrated chromium hydroxide; step (d) corresponds to its dissolving in excess $NaOH$.



When acid is added to a solution such as in equation (d), the above set of reactions is progressively reversed, first causing precipitation of chromium hydroxide by the reverse of reaction (d) and then its subsequent dissolving by the reverse of reaction (c).

Of the other fourth-row transition elements, zinc is the only element showing amphotericism. $Cu(OH)_2$ and $Co(OH)_2$ will dissolve in very strong alkali, but hydroxides of iron, nickel, and

manganese are practically insoluble. The subject has some relevance because of the complex ions formed.

This idea of amphotericism is related to the Bronsted theory of acids. We could say (although we do not often do so) that HSO_4^- or even H_2O is "amphoteric." Each can act as an acid or base.

The distribution of amphoteric behavior of hydroxides other than $Cr(OH)_3$ is shown by the following portion of the Periodic Table.

		Al good	Si none	P none	S none
Cu poor	Zn good	Ga good	Ge fair	As fair	Se none (?)
Ag poor	Cd poor	In fair	Sn good	Sb fair	Te none (?)
Au poor	Hg none	Tl none	Pb good	Bi none (?)	Po (?)

The amphoteric qualities of these elements are not restricted to aqueous systems.

Answers to Exercises and Problems

Exercise 20-1

Use Figure 20-1 to decide which orbital would be used after the $3d$ orbitals have been filled. What element has this configuration? In which family does this element occur?

Answer

The electrons will go into the $4p$ orbitals after the $3d$ orbitals have been filled, giving gallium, in family three. The student can decide which family by using the Periodic Table.

Exercise 20-2

Use Figure 20-1 to decide what the electronic configuration for yttrium ($Z = 39$) would be. Would you expect yttrium to have chemical properties more like aluminum or scandium?

Answer

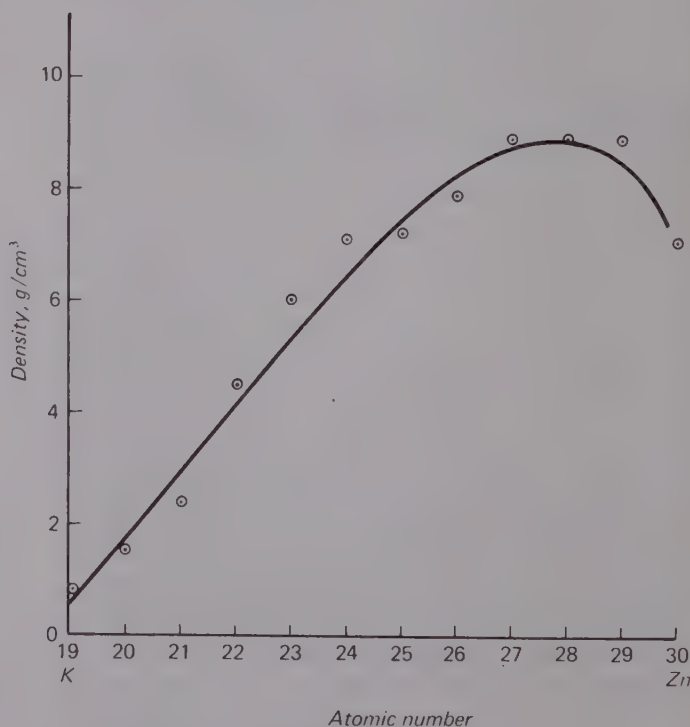


Expect properties like scandium.

Exercise 20-3

The densities for metallic K and Ca are 0.86 g/cm^3 and 1.55 g/cm^3 , respectively. Use information from Table 20-2 to draw a graph of density versus atomic number for the elements K through Zn. Does your graph suggest a regularity?

Answer to Exercise 20-3.



There is generally an increase in density from K to Cu.

Problem 1

Why are the elements with atomic numbers 21 to 30 placed in a group and considered together in this chapter?

Answer

The valence electrons of all these elements are in $4s$ and $3d$ orbitals. This makes their chemical behavior similar. They are grouped together

because, by noting the generalities of the group, we are able to express a great deal of information in a few statements.

Problem 2

- (a) chromium,
(b) molybdenum,
(c) tungsten.

Write the orbital representation for

Answer

The student may assume that the sd^5 electron pattern of Cr holds throughout. Actually it does not. It does for Mo, but for W the

energy of the $6s$ orbital is sufficiently less than that of a $5d$ orbital such that the $6s$ orbital remains filled rather than require an electron shift to half-fill the five $5d$ orbitals.

Cr	At. No. 24	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6$	$4s^1 3d^5$				
Mo	At. No. 42	Same as Cr			$3d^{10}$	$4s^2 4p^6$	$5s^1 4d^5$		
W	At. No. 74	Same as Mo					$4d^{10} 4f^{14}$	$6s^2 5d^4$	

Problem 3

What properties of the transition elements are consistent with their being classified as metals?

Answer

The following properties are consistent with the classification of transition elements as metals:

(a) They are good electrical and thermal conductors.

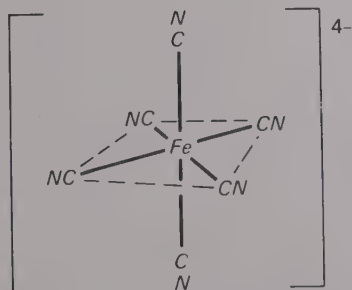
(b) They are lustrous and have high tensile strength.

(c) They have many valence orbitals for bonding. Note also that the ionization energies given (in Textbook Table 20-2) are relatively low.

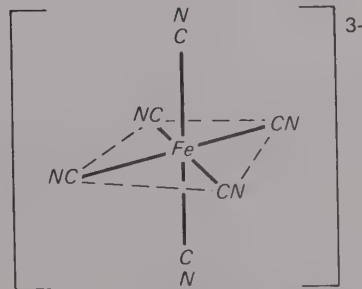
Problem 4

Ferrous ion, iron(II), forms a complex with six cyanide ions, CN^- ; the octahedral complex is called ferrocyanide.

Ferric ion, iron(III), forms a complex with six cyanide ions; the octahedral complex is called ferricyanide. Write the structural formulas for the ferrocyanide and the ferricyanide complex ions.

Answer

$Fe(CN)_6^{4-}$
Ferrocyanide ion

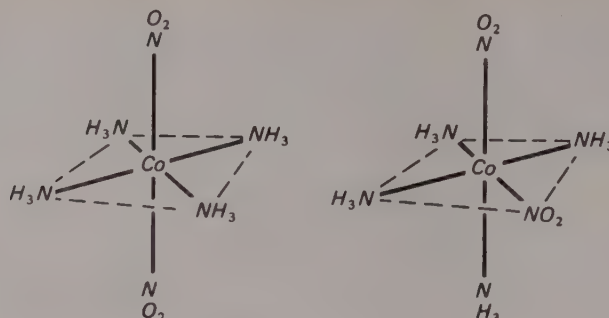


$Fe(CN)_6^{3-}$
Ferricyanide ion

Problem 5

Draw the different structures for an octahedral cobalt complex containing four NH_3 and two NO_2 groups.

Answer

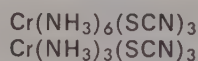


These are the only two unique forms. That is, it is not possible to make them exactly the same (superimposable). Students often draw others which can be rotated into one of these. The most common flaw is that the octahedron

is not kept symmetrical. The NO₂ groups will be either opposite or adjacent. No other possibilities exist that have regular octahedral symmetry. The use of a ball-and-stick model will clarify this.

Problem 6

Draw the structures of the compounds

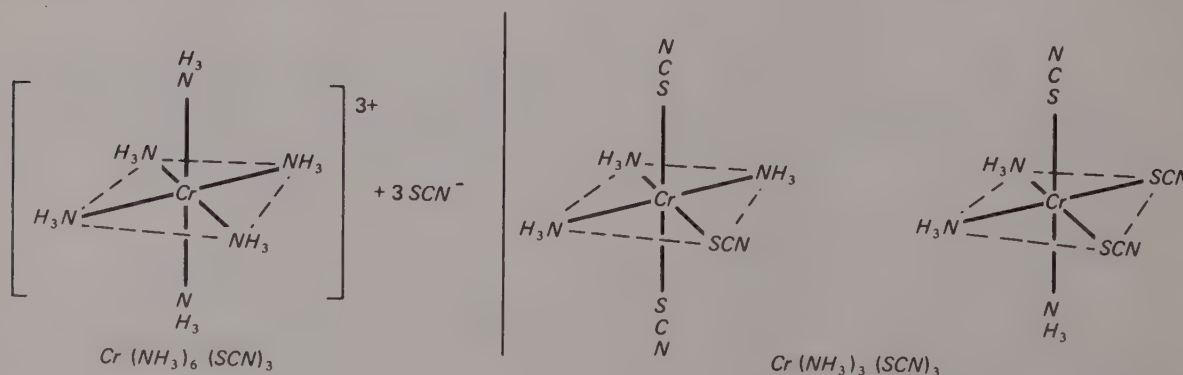


(SCN⁻ is the thiocyanate ion). Consider the oxidation

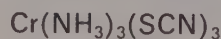
number of chromium to be +3 and the coordination number to be 6 in both compounds. Estimate

- the solubility of these compounds in water;
- their relative melting temperatures;
- the relative conductivity of the liquid phases.

Answer

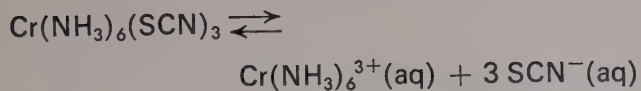


Note that the two structures given for

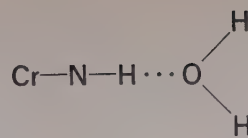


are position isomers. There are no others as long as the complex has perfect octahedral symmetry.

With a given coordination number of 6 for Cr, it is easy to suggest that $\text{Cr}(\text{NH}_3)_6(\text{SCN})_3$, hexamminechromium(III) thiocyanate, is an ionic substance;



Solubility will depend upon a balance of two factors: the energy required to tear the ions from the crystal and the energy released when the ions become hydrated. The opportunities for hydrogen bonding,



will add to the energy released.

With a coordination number of 6 for Cr, $\text{Cr}(\text{NH}_3)_3(\text{SCN})_3$, triamminetrithiocyanatochromium(III), will form a molecular solid. Solubility will depend upon the same factors as given above. The weak van der Waals forces between molecules will be easy to overcome, but the solvation energy might not be so high. There are fewer opportunities for hydrogen bonding.

Problem 7

Why does NH_3 readily form complexes, but NH_4^+ does not?

Answer

Recall that NH_3 has a pair of electrons that is not used in bonding but which can be if suitable orbitals are available on another particle. The ion NH_4^+ has neither unused electrons nor

unused orbitals. It can attract negative particles, but its one plus charge is spread over such a large surface that the attraction is not strong enough to withstand much thermal agitation. No stable complex is formed.

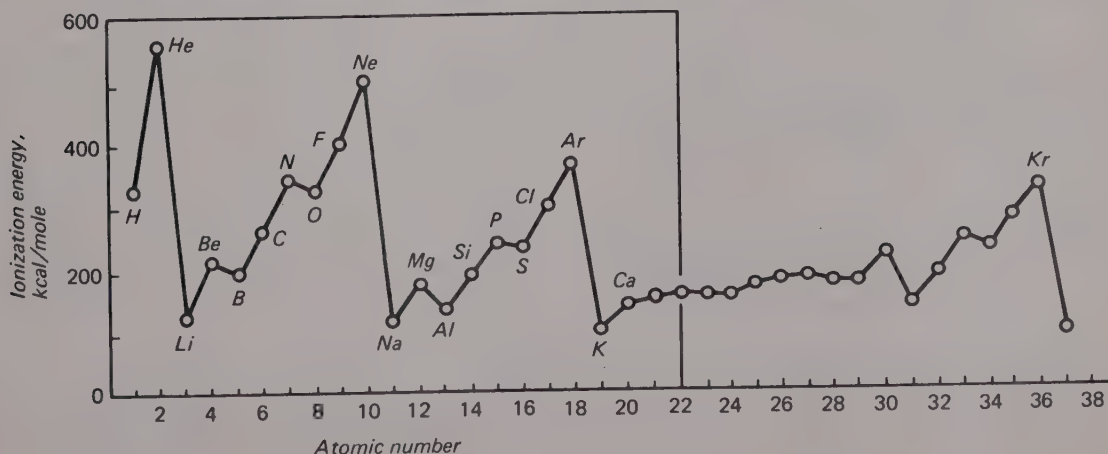
Problem 8

Place a piece of paper over Figure 9-16 and trace it. Extend the x axis and add the ionization energies of the

transition elements. Complete the row with the following ionization energies: Ga, 138; Ge, 187; As, 242; Se, 225; Br, 273; Kr, 322; Rb, 96 kcal/mole.

Answer

Contrast between ionization energy of the fourth-row transition elements and the first twenty elements.



The point of making this plot is to show the constancy of the first ionization energy of the transition metals. The characteristic rise of E_1 across the first three rows is interrupted as the

d orbitals fill. The same phenomenon occurs in the lower transition series. This constancy of E_1 is an important basis for explaining the similar properties of the transition metals.

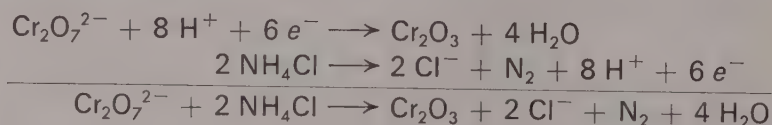
Problem 9

Chromic oxide, Cr_2O_3 , is used as a green pigment and is often made by the reaction between $\text{Na}_2\text{Cr}_2\text{O}_7$ and

NH_4Cl to give Cr_2O_3 , NaCl , N_2 , and H_2O . Write a balanced equation and calculate how much pigment can be made from 1.0×10^2 kg of sodium dichromate.

Answer

The equation can be balanced by inspection or as follows



Add Na^+ to complete.

$$(\text{g}) \left(\frac{\text{moles}}{\text{g}} \right)$$

$$(1.0 \times 10^5) \left(\frac{1}{262} \right) = 3.8 \times 10^2 \text{ moles } \text{Na}_2\text{Cr}_2\text{O}_7$$

$$(\text{moles } \text{Na}_2\text{Cr}_2\text{O}_7) \left(\frac{\text{moles } \text{Cr}_2\text{O}_3}{\text{mole } \text{Na}_2\text{Cr}_2\text{O}_7} \right)$$

$$(3.8 \times 10^2) \left(\frac{1}{1} \right) = 3.8 \times 10^2 \text{ moles } \text{Cr}_2\text{O}_3$$

$$(\text{moles}) \left(\frac{\text{g}}{\text{mole}} \right) = \text{g}$$

$$(3.8 \times 10^2)(152) = 5.8 \times 10^4 \text{ g or } 58 \text{ kg } \text{Cr}_2\text{O}_3$$

Problem 10

What is the oxidation number of manganese in each of the following: MnO_4^- , Mn^{2+} , Mn_3O_4 , MnO_2 , $\text{Mn}(\text{OH})_2$, MnCl_2 , MnF_3 ?

Answer

The oxidation number of manganese in

$$\text{MnO}_4^- \quad \text{is} \quad +7;$$

$$\text{Mn}^{2+} \quad \text{is} \quad +2;$$

$$\text{Mn}_3\text{O}_4 \quad \text{is} \quad +\frac{8}{3} \text{ (or, perhaps, } +3 \text{ for two Mn atoms and } +2 \text{ for one Mn atom, averaging } \frac{8}{3} \text{);}$$

$$\text{MnO}_2 \quad \text{is} \quad +4;$$

$$\text{Mn}(\text{OH})_2 \quad \text{is} \quad +2;$$

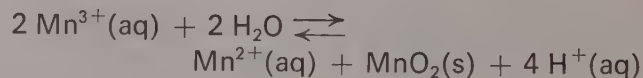
$$\text{MnCl}_2 \quad \text{is} \quad +2;$$

$$\text{MnF}_3 \quad \text{is} \quad +3.$$

Problem 11

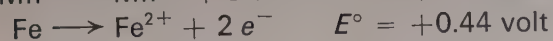
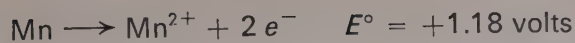
Manganese(III), Mn^{3+} , spontaneously disproportionates to Mn^{2+} and MnO_2 . Balance the equation for the reaction which occurs in aqueous solution.

Answer



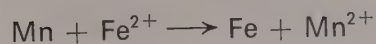
Problem 12

Use the E° values in Table 20-2 to predict what might happen if a piece of iron is placed in a 1 M solution of Mn^{2+} and if a piece of manganese is placed in a 1 M solution of Fe^{2+} . Balance the equation for any reaction that you feel would occur to an appreciable extent.

Answer

Manganese will react with Fe^{2+} , producing Mn^{2+}

and coating the Mn with metallic iron:



Fe will not react with Mn^{2+} .

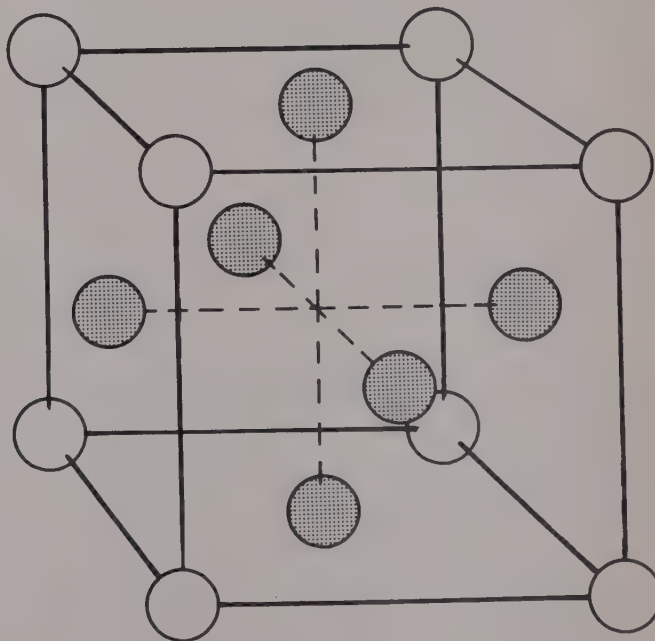
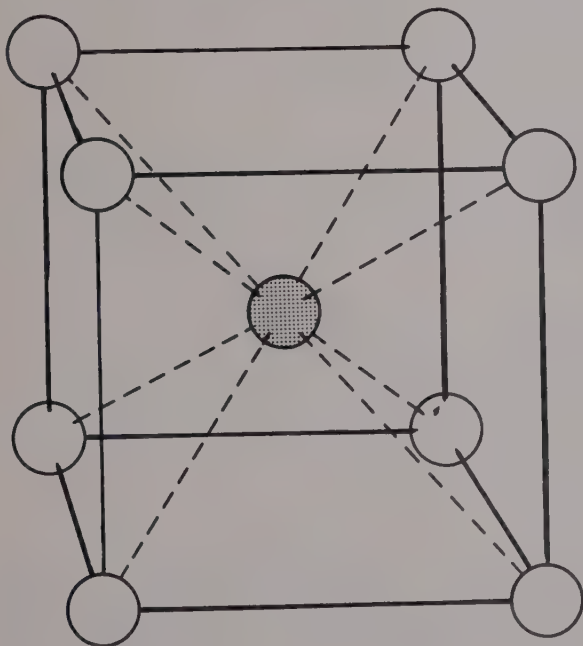
Problem 13

Iron exists in one cubic crystalline form at 20°C (body centered cubic, with cube edge length $2.86 \text{ \AA}$) and in another form at 1100°C (face centered cubic, with cube edge length $3.63 \text{ \AA}$).

- (a) Draw a picture of each unit cell, showing the nine atoms involved in a body centered cubic cell and the fourteen atoms involved in a face centered cubic cell. (See Figures 17-20 and 17-21.)

Answer

(a)



(b) See answer to (a).

(c) Body-centered: $8(\frac{1}{8}) + 1(1) = 2$.

Face-centered: $8(\frac{1}{8}) + 6(\frac{1}{2}) = 4$.

(d) Body-centered: $(2.86 \times 10^{-8})^3$

$$= 2.34 \times 10^{-23} \text{ cm}^3$$

$$\begin{aligned}\text{volume per atom} &= \frac{2.34 \times 10^{-23}}{2} \\ &= 1.17 \times 10^{-23} \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\text{Face-centered: } (3.63 \times 10^{-8})^3 \\ &= 4.80 \times 10^{-23} \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\text{volume per atom} &= \frac{4.80 \times 10^{-23}}{4} \\ &= 1.20 \times 10^{-23} \text{ cm}^3\end{aligned}$$

- (e) The "size" of an iron atom is fairly independent of the type of packing.

Note: The May 1961 issue of *J. Chem. Education*, p. A357, gives the details of a demonstration involving this change of form.

Problem 14

One of the important cobalt ores is



How much of this ore is needed to make 1.0 kg of Co?

Answer

$$\begin{aligned}(\text{kg Co}) \left(\frac{\text{moles Co}}{\text{kg Co}} \right) \\ (1.0) \left(\frac{1}{59 \times 10^{-3}} \right) = 17 \text{ moles Co wanted}\end{aligned}$$

$$(\text{moles Co}) \left(\frac{\text{moles ore}}{\text{moles Co}} \right)$$

$$17 \times \frac{1}{3} = 5.7 \text{ moles ore}$$

$$(\text{moles ore}) \left(\frac{\text{kg ore}}{\text{mole ore}} \right)$$

$$5.7 \times \frac{0.460}{1} = 2.6 \text{ kg ore needed}$$

Problem 15

Nickel carbonyl, $\text{Ni}(\text{CO})_4$, boils at 43°C , and uses the sp^3 orbitals of Ni for bonding. Give reasons to justify the following:

- it forms a molecular solid;
- the molecule is tetrahedral;
- bonding to other molecules is of the van der Waals type;
- the liquid is a nonconductor of electricity;
- it is not soluble in water.

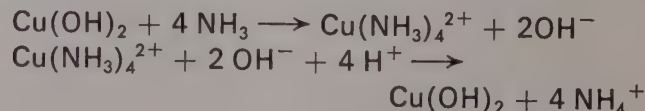
Answer

- The low boiling temperature is consistent with a molecular solid structure.
- The use of sp^3 orbitals in bonding results in tetrahedral geometry.
- Again, the low boiling temperature suggests a molecular solid in which van der Waals forces are the main ones between molecules.
- Bonding involving sp^3 orbitals is highly directive and largely covalent. Therefore ionization in the liquid is unlikely, and a nonconductor is expected.
- The lack of water solubility is consistent with the lack of polarity of the symmetrical tetrahedral molecule.

Problem 16

Write balanced equations to show the dissolving of $\text{Cu}(\text{OH})_2(\text{s})$ on the addition of $\text{NH}_3(\text{aq})$, and also the reprecipitation caused by the addition of an acid.

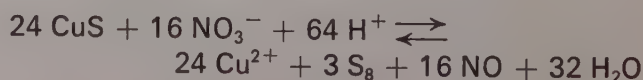
Answer



Problem 17

Cupric sulfide, copper(II) sulfide, reacts with hot nitric acid to produce nitric oxide gas, NO, and elemental sulfur. Sulfur and nitrogen are the only elements whose oxidation numbers change. Write the balanced equation for the reaction.

Answer



Radioactivity and Nuclear Changes



Intent and Approach

This chapter gives a brief view of the types of changes which occur in the atomic nucleus. Although these reactions consume or produce tremendous quantities of energy, create new elements or isotopes, and often give radioactive substances, no new principles are introduced.

This branch of science is one of high activity which may lead to far-reaching discoveries about the nature of matter. At present it is too complex to allow more than very brief coverage of some of the simplest concepts.

Outline

The mass spectrograph is described (21-1). Its use for distinguishing isotopes is covered.

Section 21-2 establishes the notation used in nuclear equations.

The three most frequently found emissions (α , β , and γ rays) from naturally radioactive nuclei are described both individually and as part of the decay series that starts with ${}^{238}_{92}\text{U}$ (21-3). Half-life is defined.

Nuclear change can be induced by bombardment (21-4). Often such reactions lead to nuclides not found naturally.

Nuclear stability is related to the neutron/proton ratio (21-5). The great energy of nuclear changes

is related to the change of mass.

Section 21-6 draws a comparison between chemical reactions and nuclear reactions. Both are shown to require collisions of particles of sufficient energy to form an activated complex. This unstable species can reform the reacting entities or give new species.

One way to determine the age of the earth depends on measurement of radioactive decay. Section 21-7 discusses two such methods.

Some uses of uncommon nuclides, with and without radioactivity, are given in Sections 21-8 and 21-9.

SCHEDULE AND RELATED MATERIAL

Suggested Time: 7 days

Text Section	Topic and Related Work	Exercises	Problems		
			Easy	Medium	Hard
21-1	The Mass Spectrograph and Isotopes	1, 2		1, 2	
21-2	Nuclear Changes	3			3
21-3	Radioactive Decay		5	4, 6	7
21-4	Nonspontaneous Nuclear Reactions			8	
21-5	Nuclear Stability		9		
	<i>Film:</i> The Transuranium Elements				
21-6	Comparison of Chemical and Nuclear Reactions			10	
21-7	The Age of the Earth				
21-8	Radiocarbon Dating			11	
21-9	Isotopic Tagging				

New Concepts

1. Half-life

2. Types of nuclear reactions

Development

21-1 The Mass Spectrograph and Isotopes

Isotopes have been covered, Textbook p. 136.

21-2 Nuclear Changes

Use this section primarily to show the notation to the student. The position of the various numbers is crucial. The code is

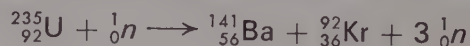
mass number **M** charge (if any)
atomic number atoms/molecule

Thus, ${}^{14}_7\text{N}_2$ is a particular nitrogen molecule made of two atoms each having a nucleus of mass number 14. Another molecule might have ${}^{14}_7\text{N}$ - ${}^{15}_7\text{N}$. Such "mixed" molecules do exist and can be detected by the mass spectrograph. Chlorine is an outstanding example because the 35 and 37 mass-number nuclides both occur naturally in substantial proportion.

The symbolism is extended to electrons, ${}_{-1}^0e$, positrons, ${}_{+1}^0e$, and neutrons, ${}_0^1n$, although these particles do not have "atomic numbers" in a strict sense. The charge of the particle is shown at the lower left.

The student will be helped in later sections if he learns that mass number and charge are conserved in the known nuclear reactions. This regularity will help him balance nuclear equations.

Note that most books and articles on nuclear reactions use an even more compact notation than the Textbook does. The example reaction



would be shown as ${}^{235}\text{U}(n,3n){}^{141}\text{Ba}, {}^{92}\text{Kr}$. The parentheses enclose the reactant nucleon separated from the product nucleon by a comma. The atomic numbers are often omitted as they can be deduced from the symbols.

21-3 Radioactive Decay

The important concepts from this section are the decay series and half-life. The first will be used later (Section 21-7) to estimate the age of the earth. Half-lives are needed in making calculations from tracer experiments (Section 21-8).

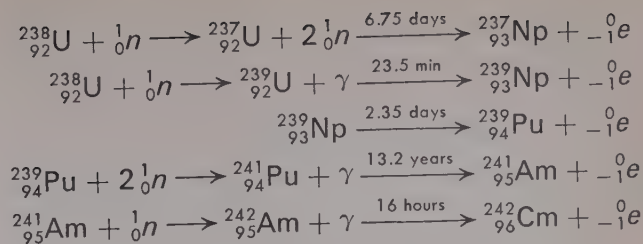
The decay of a sample of radioactive material is a statistical process. During the time $T_{1/2}$, half of the parent nuclei will change. It is not possible to predict when a particular nucleus will act. Only in a probability sense can any statement be made. During the duration of one half-life the atom has a 50% chance of converting to the product.

One rule of thumb is that a radioactive sample should be used before 10 half-life periods have elapsed. At that time there will be $(1/2)^{10}$ or $1/1024$ of the original material remaining. This same generality shows why radioactive wastes are a problem. If the half-life is only 10 years, the material might still be a hazard 100 years from now. Of course some half-lives are much longer. Those materials give even more problems. Most such wastes are dropped into the ocean depths in cement covered containers or pumped into porous, underground regions.

21-4 Nonspontaneous Nuclear Reactions

Some historic bombardment reactions are described. Figure 21-4 shows why neutrons are able to react so much more readily than protons or other charged particles. On the other hand, neutral neutrons cannot be accelerated by electric fields. Thus high energy accelerators and piles with high neutron flux play complementary roles in nuclear research. Nuclear explosions provide one way to achieve enormous neutron fluxes. In underground explosions (such as the Cyclamen test by the AEC), for instance, about 1×10^{25} neutrons/cm² were produced in 10^{-6} sec. The resulting caldera, or depression, in the ground at the test site is 275 feet in diameter and 55 feet deep.

Some of the main reactions used to produce transuranium elements are shown below. The half-lives of spontaneous reactions are shown over the arrows.



Many of these elements, unknown 30 years ago, are now made to order, sometimes in large quantities. Approximately 4 tons of ${}^{242}\text{Pu}$ is used yearly for nonweapon use (mainly in power reactors). The metal is made from PuF_4 by reduction with Ca(g) . The metal is the most complex one known. It exists in six modifications whose densities vary from 19.8 to 15.9 g/cm³. This last type, called *delta plutonium*, shrinks when heated.

21-5 Nuclear Stability

This section must be presented at a rather empirical, or descriptive, level. The theories of the nucleus are either too simple to fit the facts well or too complicated for beginning students. The following paragraphs contain an extremely simplified summary of ideas about the nucleus.

The forces between nucleons are known to be:

1. short range, about 10^{-13} cm in extent. The nuclei of all atoms have about the same density. If the forces operated over long distances, the nuclei with many particles would be denser than those of few particles.
2. strong, about 5 million times the forces in chemical bonds.
3. strongly dependent on distance. They go from practically zero to very attractive and on to quite repulsive as the distance between the nucleons changes from 2×10^{-13} to 0.4×10^{-13} cm.
4. independent of charge.

There are two main theories to explain these facts and the properties of nuclides. The *liquid drop* theory uses a drop of liquid as its model. The nucleons are imagined as moving much as the molecules in a sphere of liquid. This theory

(proposed by Niels Bohr and John Wheeler) applies best to excited nuclei. For instance, nuclear fission is modeled by a spherical drop being deformed to a dumbbell shape, followed by one of two processes. The dumbbell can oscillate back and forth *or* it can break into two or more fragments. These fragments usually undergo further adjustments in their n/p ratio to improve their stability. They do this by emitting neutrons or by β decay. The latter process is equivalent to changing a neutron to a proton so that it gives a bigger change of n/p than just loss of a neutron does.

The other main theory is called the *shell model* because it suggests the nucleons are arranged in energy "shells" much as electrons are. In fact, the same type of quantum-mechanical calculations are used to derive the levels. The arrangement has groups of orbitals, each possessing comparable energies but with wide gaps between the groups. The orbital diagram is complicated by a factor called *spin-orbital interaction* which causes the calculated levels to shift in a complex way. However, if the nucleons are placed into the calculated orbitals in the same manner used for electrons (Textbook p. 151, Teacher's Guide p. 152) using the same aufbau and Pauli exclusion principles, then plausible explanations are obtained for many experimental facts about non-excited nuclei. In particular, nuclei with certain "magic" numbers of nucleons represent filling of the nuclear orbitals. These nuclei are found to be particularly stable ones, in close analogy to the noble gases for the electron filling case. These "magic" numbers are 2, 8, 20, 28, 50, 82, 126, and 184 and they apply to either protons or neutrons. Thus $^{118}_{50}\text{Sn}$ has a magic number of protons (50) while $^{89}_{39}\text{Y}$ has the same magic number of neutrons. Both are stable nuclides. Other features of this model are explained in the suggested articles and Choppin's book given under *Supplementary Material*, p. 434.

The tremendous energies obtained from fission or fusion are probably known to your students. Nuclear reactors based on fission processes are being used as power sources for electricity generation and naval vessels. At the end of 1966

there were 56 civilian power stations in the United States including 40 under construction or planned. There were four military installations. These plants generate only 0.3% of the power produced in the United States. The Atomic Energy Commission predictions are for 25% by 1980.

At the start of 1967, the U. S. Navy had 66 nuclear powered submarines, plus one aircraft carrier, one cruiser, and one frigate. One nuclear cargo ship, the N.S. *Savannah*, was in operation at the end of 1966. There has been steady improvement in the cost of operating these ships. For instance, the first reactor cores in the submarine *Nautilus* delivered 62,000 miles at \$48/mile. The improved cores now available are expected to last for 400,000 miles at \$7.50/mile. The new cores planned for a second carrier will last 13 years so that the ship will need only one refueling during its lifetime.

Film, TRANSURANIUM ELEMENTS,

fits here. See p. 435 for summary.

21-6 Comparison of a Chemical and a Nuclear Reaction

Here we have made a deliberate effort to get reactions involving the same elements and to comment on three factors for each. While the difference in energy is often mentioned, there is also some value in suggesting the similarities.

21-7 The Age of the Earth

This and the next two sections give a few details of some uses of nuclear chemistry.

The list of equations in the decay scheme of ^{238}U is perhaps formidable to a beginner. An analogy may help. Draw a figure such as Figure 21-1 on the chalkboard. Be sure to get some semblance of scale into the size of the different vessels. Then ask the students to imagine that the elements are represented by this series of vessels, each of a size in proportion to the

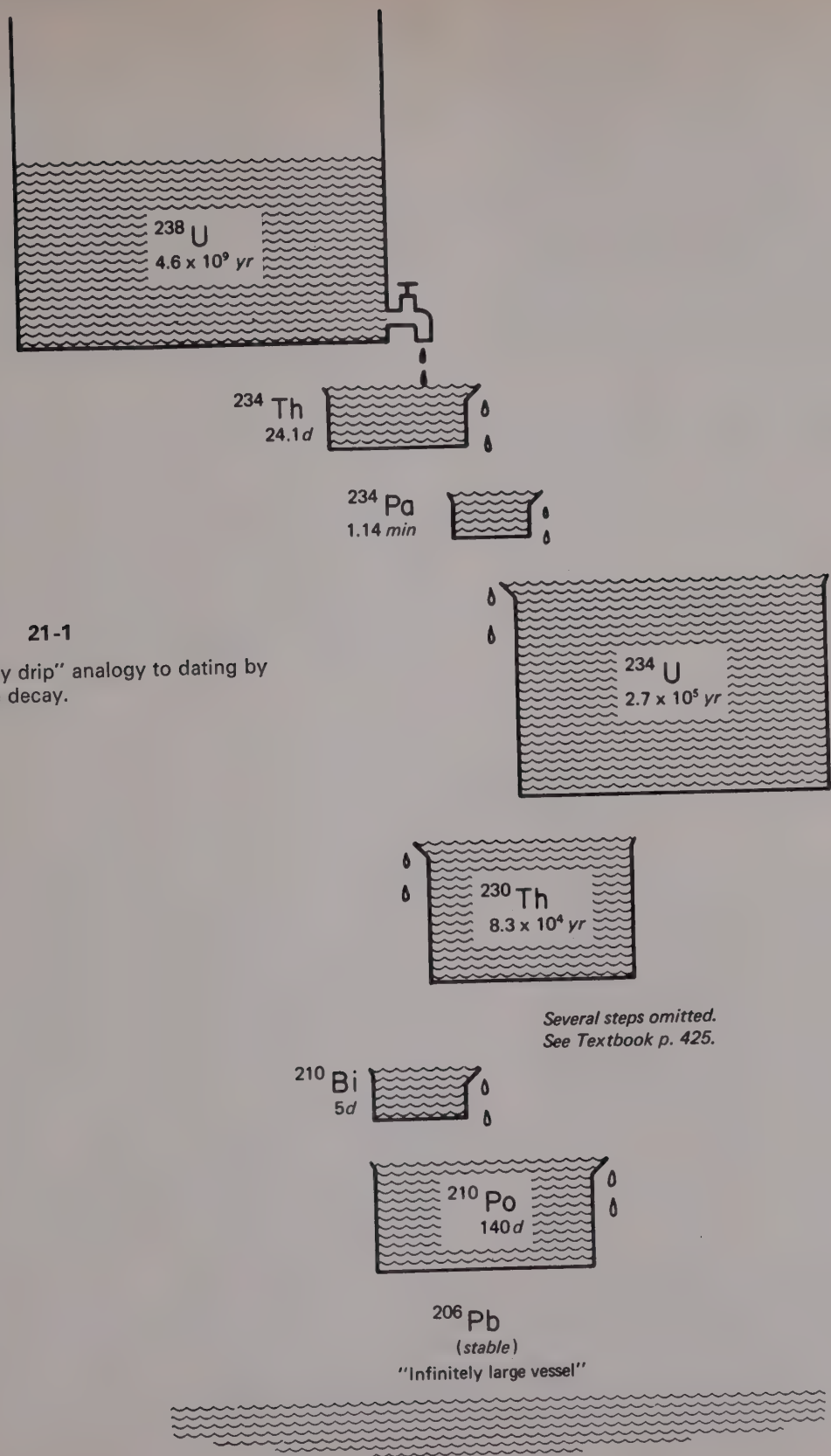


FIGURE 21-1
The "steady drip" analogy to dating by radioactive decay.

half-life of the isotope. The intermediate vessels are imagined to be full of liquid. This means we are assuming there has been sufficient time for "secular equilibrium" to be attained.

Now, the point is that when two drops of liquid (a certain number of atoms) leave the first reservoir (disintegrate), they cause two drops to overflow from the second. These eject two from the third container and so on. The final result is that two drops appear in the infinitely large, final container. The infinite size corresponds to a stable nuclide.

It is usually easy to get the student to see that the amount of liquid at the bottom depends *only* on the rate drops leave the top container. In a parallel way, the quantity of ^{206}Pb collected depends on the rate of ^{238}U decay and the time the "system" has been going. It is the half-life of ^{238}U that determines the secular equilibrium.

A simple calculation shows that ^{206}Pb does not accumulate very fast.

mass ^{206}Pb formed from 1 g ^{238}U in 10^6 years

$$= \left(\frac{1}{238}\right) (206) \left(\frac{1}{4.6 \times 10^9}\right) (10^6) \\ = 2 \times 10^{-4} \text{ g or } 0.2 \text{ milligram}$$

21-8 Radiocarbon Dating

21-9 Isotopic Tagging

These sections give a very small glimpse of the extreme usefulness of nuclei that can be identified and followed. Such applications are now made in chemistry, physics, archeology, geology, medicine, engineering, and many other areas. In addition to dating, radioisotopes are used to measure flow rates in refineries, to detect fallout, to trace the paths in numerous reactions, and to find plugs in pipelines.

Supplementary Material

Articles

The July-August 1967 issue of *Chemistry* is devoted to nuclear science. The articles are well written and at a level suitable for high school students.

"The Nuclear Force," R. E. Marshak, *Scientific American*, March 1960, p. 98.

"The Chemistry of the Actinides," L. B. Asprey and R. A. Penneman, *Chemical and Engineering News*, July 31, 1967, p. 75. This article, while somewhat technical, contains much interesting information about elements 90-103. It can be used to show the application of principles to new chemical situations.

Books

G. R. Choppin, *NUCLEI AND RADIOACTIVITY*, 1964. W. A. Benjamin, Inc., New York. This paperback contains a good selection of topics, explained in a manner suitable for beginners in the subject.

UNDERSTANDING THE ATOM is the title of a series of about 30 pamphlets distributed by the Atomic Energy Commission. Five of these most closely related to material in this chapter are titled

Plutonium, Rare Earths, Microstructure of Matter,

Radioisotopes in Industry, and Synthetic Transuranium Elements.

Single copies can be obtained free by writing to USAEC, P.O. Box 62, Oak Ridge, Tenn. 37830 and stating the proposed use of the material.

P. M. Hurley, *HOW OLD IS THE EARTH?*, The Science Study Series, 1959. Doubleday and Co., Inc., Garden City, New York. Considerable detail, but at a high school level on dating methods. Gives many results and related events.

D. J. Hughes, *THE NEUTRON STORY*, The Science Study Series, 1959. Doubleday and Co., Inc., Garden City, New York. Describes the discovery, properties, and reactions of neutrons. Not mathematical.

G. T. Seaborg, *MAN-MADE TRANSURANIUM ELEMENTS*, Prentice-Hall, Englewood Cliffs, N. J. (1963). A description, aimed at the able student, of the discovery, electronic structure, chemical properties, and nuclear reactions of elements 93-103.

The Annual Report to Congress of the Atomic Energy Commission and the Supplemental Report on Fundamental Nuclear Energy Research (\$2.25 for the latter) are available from the Superintendent of Documents, U. S. Govt. Printing Office, Washington, D. C. 20402. These reports give a summary of activities during the past year. They provide a great deal of information and contain many illustrations.

Film

For ordering information see the *List of Film Sources* at the back of the Teacher's Guide.

TRANSURANIUM ELEMENTS

A CHEM Study film

Running Time: 23 minutes

This film, produced in the Lawrence Radiation Laboratory at Berkeley, California, features four chemists who were principals in the actual discovery and identification of the transuranium elements. The collaborator, Dr. Glenn Seaborg, reviews the historical problem of the placement

of the transuranium elements in the Periodic Table, and emphasizes that the new elements must be synthesized and identified. Dr. Burris Cunningham shows in experiments that neptunium, plutonium, and americium can behave like uranium but that curium behaves like its rare earth homolog, gadolinium. Dr. Stanley Thompson demonstrates how the ion-exchange separation technique aids in identification, using actual solutions of curium, berkelium, californium, and einsteinium. Albert Ghiorso demonstrates the Hilac, an instrument used in making elements of very high atomic number. He discusses the methods which helped lead to the discovery of elements 102 and 103 and proposes a similar type of reaction which has led to the discovery of element 104.

Background Discussion

The Origin and Abundance of the Elements

What is the origin of the universe?

How did life develop on the planet Earth?

Questions like these have intrigued philosophers and scientists for thousands of years. Although answers cannot yet be presented, tentative explanations have been proposed for these and related questions. The experimental observations and measurements come from a variety of fields. In this section two areas will be outlined that may someday lead to an understanding of the important questions given above. Initially these topics may seem unrelated.

First consider Figure 21-2 which shows the relative abundance of the elements in the universe. These numbers do not apply to the Earth alone but to a much larger sample, including the stars and the material between. The general decrease in abundance as one proceeds from the atoms with smallest mass to those with high molar mass is shown by the shaded band in this graph. There are several important points to be emphasized:

Hydrogen is the most abundant element in the universe. It is about ten times more abundant than helium which, in turn, is ten times more abundant than any other element. The composition of the universe is 90% H and 9% He and 1%

all other elements.

Lithium, beryllium, and boron are less abundant than expected by a factor of about 10^7 .

Iron and its neighboring elements are more abundant by a factor of 10–100.

Any proposal to explain the origin and the abundance of the elements should give at least qualitative agreement with these anomalies.

Now consider Figure 21-3 which is called the Russell-Hertzsprung diagram. In the early 1900's astronomers began to catalog stars by plotting their color (or surface temperature) against their absolute luminosity (or energy production). Instead of a random distribution, the observations showed some striking regularities. Most stars are located in a narrow band in this diagram, a band often referred to as the Main Sequence. A few stars are placed in the upper right corner and a few stars are placed in the lower left corner. Astronomers refer to these as Red Giants and White Dwarfs; for the moment we will ignore them.

Several points are of interest for our discussion. Our star, the Sun, falls in the Main Sequence of stars; it is not an unusual star. The hottest stars have the highest luminosity. This means they are producing energy at a very high rate. The coolest stars are least luminous and are producing energy at a very low rate.

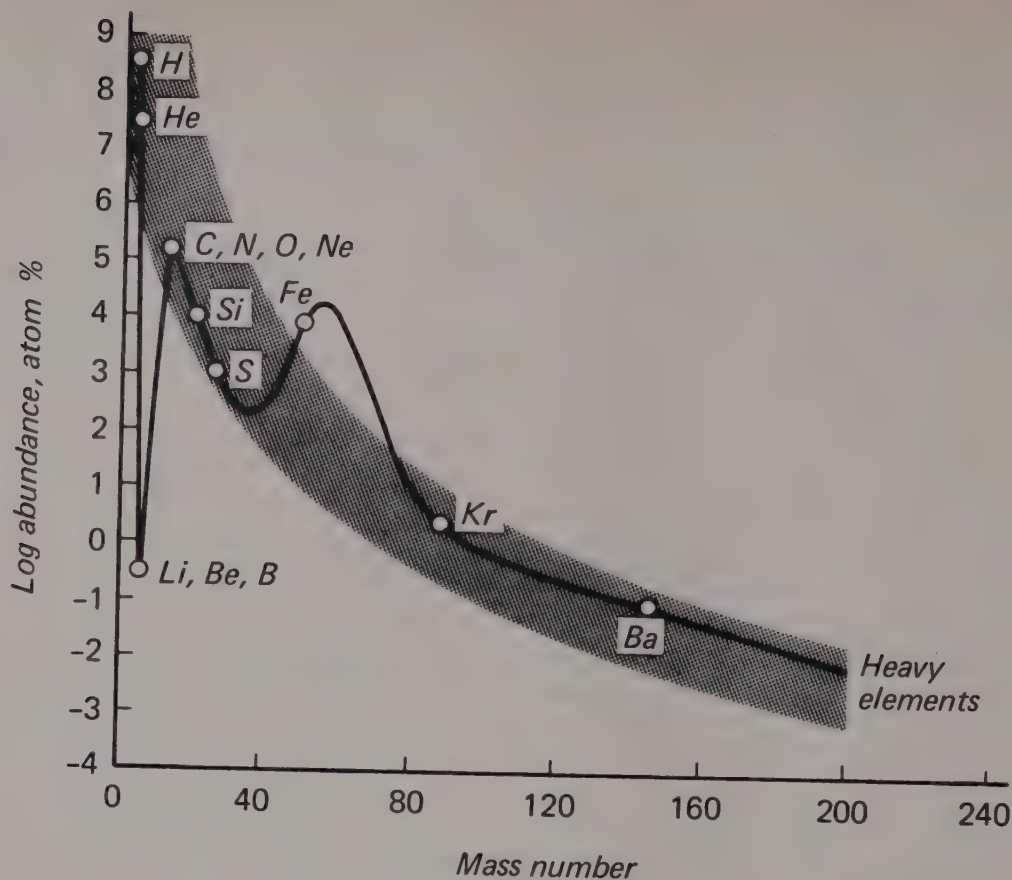


FIGURE 21-2

Cosmic abundance of the elements ($\text{Si} = 10^4$ as reference).

The regularity in this diagram invites an explanation. Sir Arthur Eddington presented a model which has been widely adopted. Eddington showed that only two parameters need enter into the process of placing a star in this diagram. The total mass of the star and its chemical composition must be known. The mechanism of energy production does not enter into the calculation. Briefly Eddington's model proposes these stages in the life history of a star.

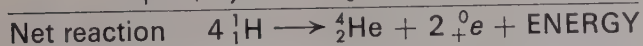
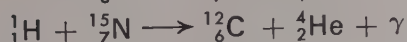
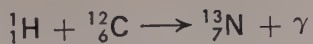
1. Vast clouds of hydrogen are slowly pulled together because of gravitational forces. The potential energy of matter in the gravitational field is converted into kinetic or thermal energy and the temperature increases.
2. Ultimately some energy-producing mechanism begins in the star. There is then a balance between thermal energy outflow and energy

input from matter collapsing under the influence of gravitational forces. This balance can exist for millions and billions of years. The star is on the Main Sequence as long as this steady state can be maintained.

3. The Red Giants and White Dwarfs may have different chemical composition from Main Sequence stars. They also may indicate either very early or very late stages of the lifetime of a star.

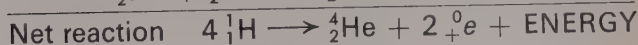
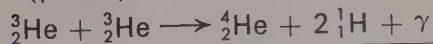
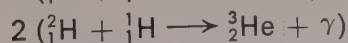
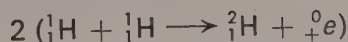
Eddington's calculations did not depend on how a star produced energy. It was not until 1938 that Hans Bethe suggested a detailed mechanism for energy production. Two different sets of nuclear reactions are offered to explain how Main Sequence stars produce energy. The net reactions are identical and are referred to as hydrogen "burning" reactions.

The Carbon Cycle



This cycle takes about 2×10^6 years for a particular C-12 to return again as carbon-12.

The Hydrogen Cycle



On a molar basis, formation of helium from hydrogen by either of these reactions releases approximately 4×10^8 kcal. At the present time it is thought that the carbon cycle applies to stars larger and hotter than the Sun. The second

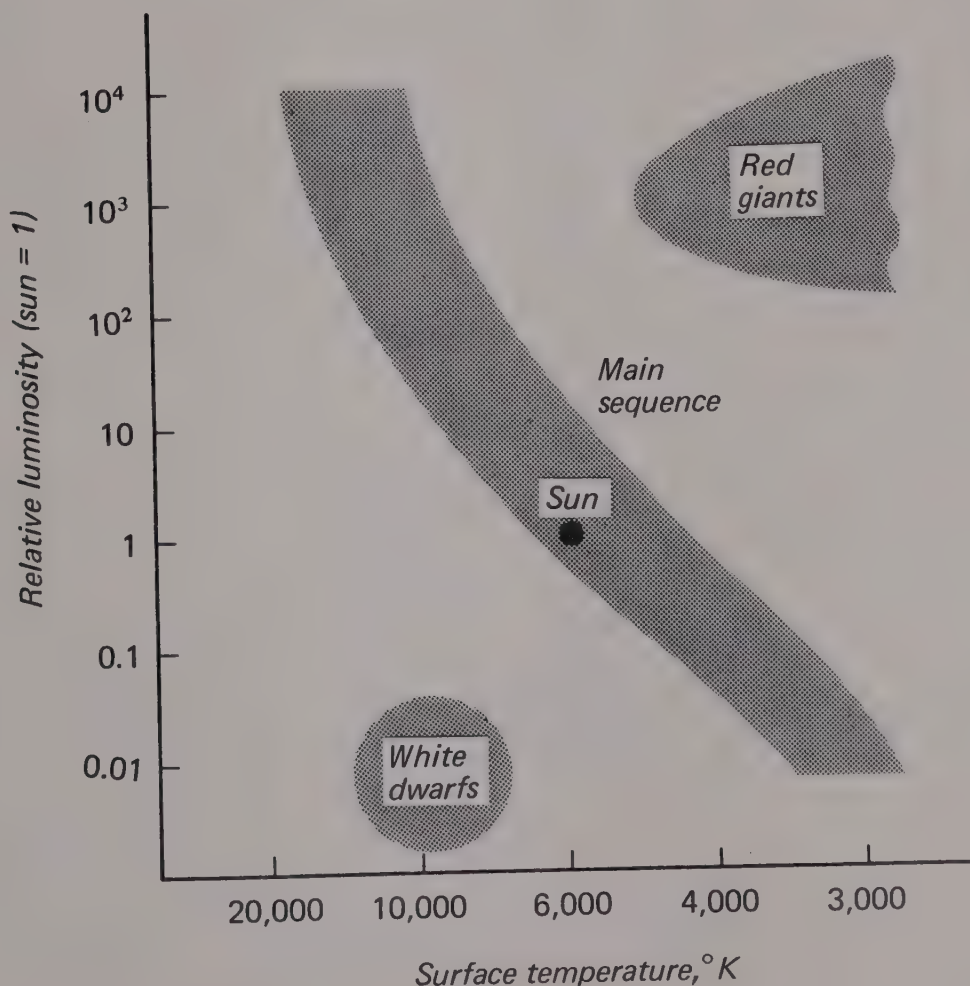


FIGURE 21-3

Classification of star types.

H-"burning" process probably describes energy production in the Sun and in stars smaller and cooler than the Sun.

Bethe offered no explanation for the Red Giants and White Dwarfs. However, additional measurements indicate that these stars are indeed very different from Main Sequence stars. Red Giants are immense stars, with densities only a millionth that of water. If placed in our Solar System, some Red Giant stars would be so large that they would include the orbit of Mars. White Dwarf stars are also quite unusual. Many are about the size of the Earth but with densities a million or even a billion times that of water.

The development of a star and the formation of the elements now appear to be closely related subjects. There have been two main theories proposed to account for the birth and death of stars and for the abundance of the elements. The first of these, primarily due to George Gamow, is called the Big Bang theory. According to it, there was some time in the past when all matter in the universe was compressed into one huge ball. Under these conditions, all protons and electrons would react to form neutrons. For some unexplained reason, this ball of neutrons expanded in a huge explosion. During the first hours or days after the explosion, a large variety of nuclear reactions could take place. Neutrons would decay into protons and various low mass nuclei could form (look back at the second group of H-"burning" reactions for some examples).

Gamow initially proposed that all of the elements would be synthesized during the first stages of the explosion. An awkward problem arises when an attempt is made to understand the details. There is no easy way to build nuclides with mass numbers greater than 8. A list of the nuclides with mass number 8 shows what the problem is.

<i>Nuclide and reaction</i>	<i>Half-life</i>
${}^8_3\text{Li} \longrightarrow {}^8_4\text{Be} + {}^0_{-1}e$	0.84 second
${}^8_5\text{B} \longrightarrow {}^8_4\text{Be} + {}^0_{+1}e$	0.76 second
But	
${}^8_4\text{Be} \longrightarrow {}^4_2\text{He} + {}^4_2\text{He}$	10^{-16} second

Almost every nuclear reaction leads to ${}^8_4\text{Be}$ which immediately carries one back to mass number 4, the very stable nucleus ${}^4_2\text{He}$. Since only a short period of time is available during Gamow's Big Bang expansion for the formation of the elements, the difficulty of bridging mass number 8 seems to argue against his proposal.

In the late 1940's and early 1950's a very different proposal, called the Steady State Theory, was advanced by Gold, Bondi, and Hoyle. This theory is based on the notion that hydrogen is formed spontaneously throughout the universe and then is brought together by gravitational forces to form stars. Ultimately during the lifetime of the stars, hydrogen is consumed in the energy producing reactions suggested by Bethe, to form helium and then the remainder of the elements. The final stages in the lifetime of a star probably involve nova or supernova explosions which return matter to the star formation cycle just outlined. The remnants of the novas and supernovas collapse under gravitational forces to the dense material called White Dwarf stars. The only way to account for these stars is in terms of nuclei being packed closer and closer together. The extranuclear electrons no longer keep nuclei apart and eventually densities as high as 10^{14} g/cm³ may be attained.

This theory suffers from the same problem at mass number 8 that Gamow's theory does. Or stating this in its reverse form, if some way to bridge mass number 8 is found in the Steady State theory, the same mechanism can be applied to the Big Bang explosion. At the present time it is not possible to decide between the two theories. Each proposes that hydrogen is formed, that stars arise when gravitational forces pull enough material together and when the temperature reaches a point where nuclear reactions provide energy to sustain a star, and that the elements are formed during various stages of the star's existence. The question of the initial phases, that is Big Bang versus Steady State, is still not resolved.

The various stages in the birth and death of a star can be summarized in a qualitative fashion. Figure 21-4 shows this development pictorially.

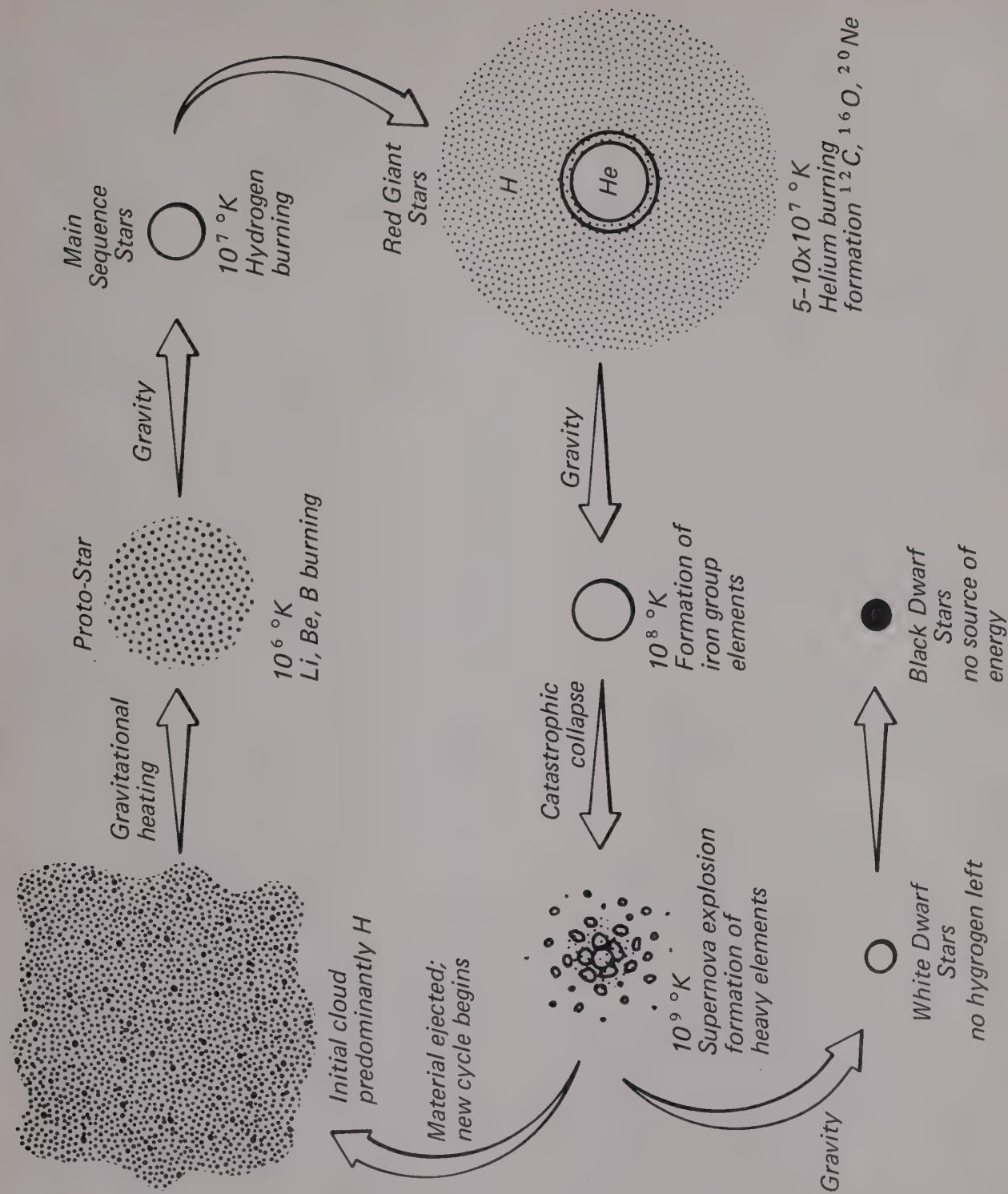
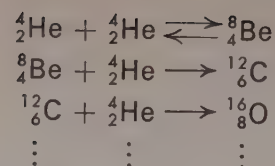


FIGURE 21-4
Birth and death of a star.

1. Gravitational forces bring together material, principally hydrogen atoms. The temperature builds up as gravitational energy is converted to kinetic energy. For a star such as the Sun, this process takes several million years.
2. At about 10^6 degrees, the light elements lithium, beryllium, and boron are consumed in nuclear reactions of the type referred to in the discussion of mass number 8. This energy source sustains a star for only a short period of time. The low abundance of these elements in the universe is explained by this hypothesis.
3. Gravitational heating continues until hydrogen "burning" reactions begin at about 10^7 degrees. This places a star on the Main Sequence. The most massive stars use up their hydrogen fuel in several million years; the least massive stars stay on the Main Sequence for perhaps 100 billion years. The Sun probably has a lifetime on the Main Sequence of 10 billion years. Since it is only about 5 billion years old, there is little danger of its running out of gas for a while.
4. As hydrogen is consumed, the center of the star grows richer in helium. Energy production *via* the hydrogen "burning" reactions takes place at a spherical shell while very unusual things happen to the center of the star. The temperature increases to perhaps 10^8 degrees and matter is packed so close together that Newtonian mechanics no longer applies. Quantum mechanics must be used to deal with stellar structure. The consequence of this is that the outer layers of the star expand to balance the temperature rise in the interior. A Red Giant forms with very low density and with relatively low surface temperature. At the center of such a star, helium "burning" occurs and a way to create elements of mass number larger than 8 is finally achieved. The steady state concentration of ${}^8_4\text{Be}$ is very low, but there are millions of years during which the occasional reactions leading to ${}^{12}_6\text{C}$ can take place.



The nuclei which are multiples of ${}^4_2\text{He}$ are formed up to perhaps ${}^{40}_{20}\text{Ca}$. One would expect their abundance to drop off exponentially and this is seen in an approximate fashion in Figure 21-2. The lifetime of a star in the Red Giant phase has been estimated as 1–100 million years.

5. After the helium in a star has been consumed, gravity collapse causes further heating to about 10^9 degrees. A variety of nuclear reactions occur, depending to some extent on the original mass of the star. Hoyle has shown that under certain circumstances the production of the iron-group nuclides is strongly favored. These are the most stable of all nuclides and their high abundance in the universe is easy to understand.
6. The final stages in the life of the star take place rapidly. Gravity continues to play a major role and the temperature increases to the point where endothermic reactions can occur, leading to the formation of the elements beyond iron, up to bismuth. In large enough stars, the rates of these reactions are so high that gravitational collapse occurs. The outer layers of a star, still quite rich in hydrogen, fall into regions of very high temperatures. The rate of energy production is so great that the star literally blows apart in a supernova explosion. In the very short time interval of a supernova explosion (up to a few minutes), elements up to and beyond bismuth form. One hypothesis today is that ${}^{254}_{98}\text{Cf}$ forms in the supernova explosion and accounts for its energy emission which has a half-life of approximately 55 days.
7. The remnants of the supernova are pulled by gravitational forces into a more and more dense configuration. The star is not large enough to undergo again the reactions given in part 6. Almost all hydrogen has been used up and the star has exhausted its nuclear fuels.

This is the White Dwarf stage, using up the last of the gravitational energy that the star began with. Ultimately the White Dwarf cools down to become a Black Dwarf and ceases to be observable from the Earth.

This intriguing story of the life history of a star suggests that the Sun and its set of planets must be at least a second generation system. The first generation stars must be pure hydrogen and of course would not have planets. The fact that there are radioactive elements such as thorium and uranium in the earth's crust strongly suggests that the material in the Solar System must have come from supernova explosions in the past.

Chemists and biochemists are speculating today about the origin of life on the Earth. They start with the origin of the Sun that we have just outlined and propose different models that lead to first simple and then complex molecules. Measurements of the atmospheres of Mars and Venus, recently accomplished by the space experiments of groups in the United States and in Russia, have led to some changes in the detailed models. The story of the formation of stars, the energy producing reactions, and the formation of the chemical elements is leading directly to explanations of the beginning of life on the planet Earth and presumably on millions of other planets in the Universe.

Answers to Exercises and Problems

Exercise 21-1

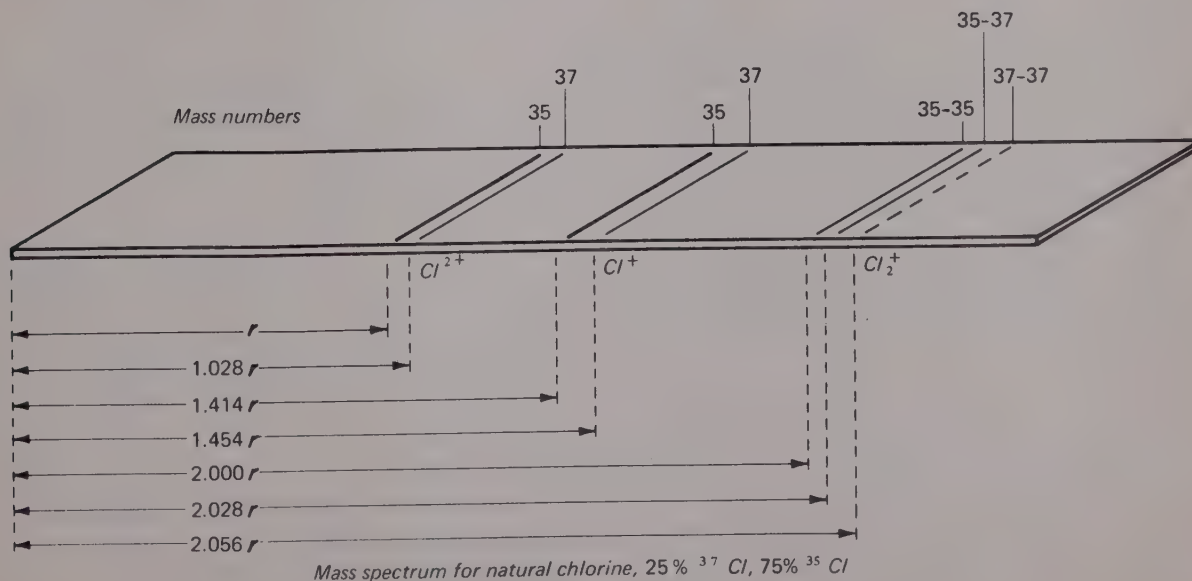
When chlorine, Cl_2 , is examined in a mass spectrograph, Cl_2^+ , Cl^+ , and Cl_2^{2+} ions are formed. Remembering that there are two isotopes of chlorine, ^{35}Cl (75%)

and ^{37}Cl (25%), describe qualitatively the appearance of the mass spectrum. Which ion will produce lines at the largest radius? Which at the smallest radius? How many lines will each type of ion produce?

Answer

Qualitatively, the heaviest mass and lowest charge will be found at the largest radius (Cl_2^+), and the lowest mass and highest charge will be

found at the smallest radius (Cl_2^{2+}). Hence, if there were but one isotope, there would be three lines, as follows.



Each of these lines, however, will be influenced by the presence of two isotopes. Thus there will be a line due to $(^{35}\text{Cl})^{2+}$ and $(^{37}\text{Cl})^{2+}$. The heavier isotope, ^{37}Cl , will show the higher radius. Since there is three times as much ^{35}Cl as there is ^{37}Cl , the inner line will be three times as intense as the other. A similar pair will be obtained for Cl^+ . The species Cl_2^+ will produce three lines, due to $(^{37}\text{Cl} - ^{37}\text{Cl})^+$, $(^{37}\text{Cl} - ^{35}\text{Cl})^+$, and $(^{35}\text{Cl} - ^{35}\text{Cl})^+$. Thus the spectrum will be as shown in the second figure.

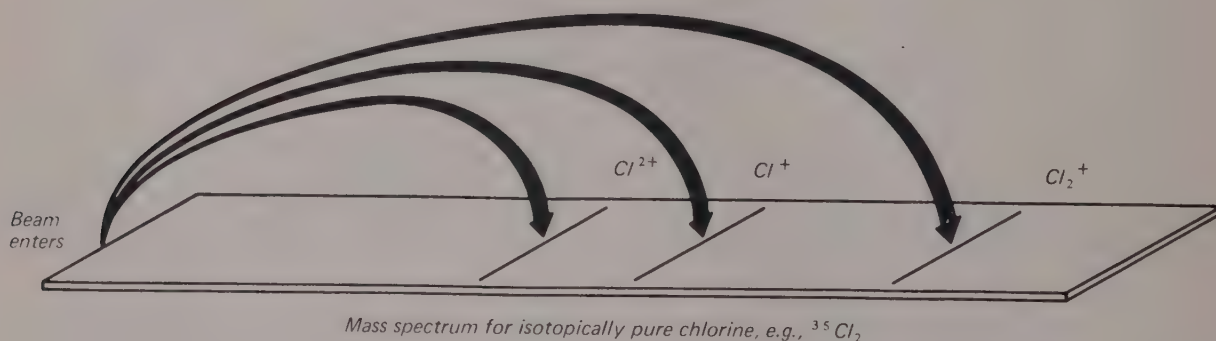
The better students may care to attempt to calculate the relative intensities of the triplet caused by Cl_2^+ . The probability of both atoms being ^{37}Cl is $\frac{1}{4} \times \frac{1}{4} = \frac{1}{16}$. The probability of

both atoms being ^{35}Cl is $\frac{3}{4} \times \frac{3}{4} = \frac{9}{16}$. The rest of the molecules, the fraction $\frac{16}{16} - \frac{10}{16} = \frac{6}{16}$, will contain one atom of ^{35}Cl and one atom of ^{37}Cl . Thus the intensities will be in the ratio 1 : 6 : 9.

Quantitatively, the radius depends upon charge and mass, as follows

$$r = \frac{1}{B} \sqrt{\frac{2Vm}{e}}$$

With this expression, the relative radii can be calculated quantitatively. The second figure shows these radii expressed in terms of the smallest observed radius, that of $(^{35}\text{Cl})^{2+}$.



Exercise 21-2

Suppose a mass spectrograph is used to measure the charge/mass ratio for fluorine ions. Fluorine has only one stable isotope and its molar mass is 19.0 grams/mole. From the measured charge/mass ratio, 5.08×10^3 coulombs/gram, and the assumption that the ion has one electron charge, calculate the mass of one ion. Use $e = 1.6 \times 10^{-19}$ coulomb. Repeat the calculation, assuming the ion has two electron charges. Now calculate Avogadro's number from the mass of a mole of fluorine ions, using each of your two calculations. Which assumption about ion charge do you prefer? Could the other be correct as well?

Answer

Since e/m is given as 5.08×10^3 coulombs/gram, and since $e = 1.6 \times 10^{-19}$, then

$$m = 1.6 \times 10^{-19} / 5.08 \times 10^3 = 3.16 \times 10^{-23} \text{ g}$$

If the measured charge/mass ratio is $2e/m$, then

$$m = \frac{2(1.6 \times 10^{-19})}{5.08 \times 10^3} = 2(3.16 \times 10^{-23}) = 6.32 \times 10^{-23} \text{ g}$$

Using e , we find that Avogadro's number is

$$\frac{19.0 \text{ g/mole of atoms}}{3.16 \times 10^{-23} \text{ g/atom}} = 6.02 \times 10^{23} \frac{\text{atoms}}{\text{mole of atoms}}$$

Using $2e$, we find Avogadro's number to be

$$\frac{19.0}{6.32 \times 10^{-23}} = 3.01 \times 10^{23} \frac{\text{atoms}}{\text{mole of atoms}}$$

The single electron charge results in a value of Avogadro's number that is consistent with a multitude of other data, thus it is an acceptable

result. It is based upon the assumption that the species detected is F^+ .

Yet the assumption of a double electron charge would be consistent with the accepted value of Avogadro's number, if the mass of the particle were also doubled. This means the species detected might be F_2^{2+} rather than F^+ , which is not unreasonable.

Exercise 21-3

According to the model developed in Chapter 8, how many nucleons are present in a uranium nucleus of mass number 235? How many protons are present? How many neutrons?

Answer

There are 235 nucleons present, 92 protons and 143 neutrons.

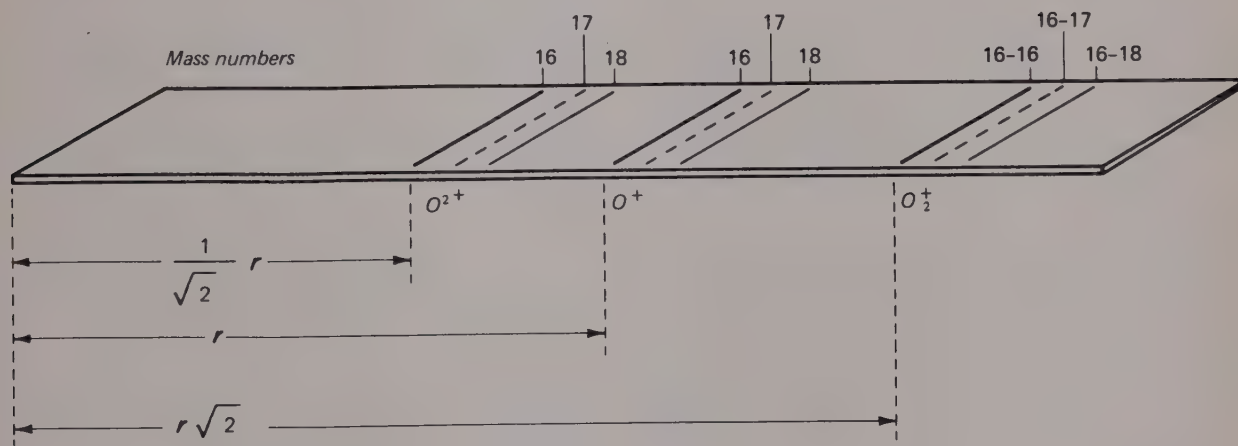
Problem 1

Describe the spectrum produced on a photographic plate in a mass spectrograph if a mixture of the isotopes of

oxygen (^{16}O , ^{17}O , and ^{18}O) is analyzed. Consider only the record for $1+$ and $2+$ ions.

Answer

The relative abundance of the isotopes can be found in Table 8-4, as ^{16}O , 99.8; ^{17}O , 0.04; and ^{18}O , 0.20. The student should certainly assume a singly and a doubly charged ion for each of the three isotopes. This assumption will lead to two sets of three lines each, as in the figure below (left and center). But if he should follow the example of chlorine he might also assume the existence of O_2^+ ions, including the various combinations of the isotopes. There are six possible combinations, but since ^{17}O and ^{18}O are so rare, lines formed by combinations containing only these isotopes would be too faint to be detectable. The visible lines due to O_2^+ ions would be due to these isotopic varieties: $(^{16}\text{O}^{16}\text{O})^+$, strong; $(^{16}\text{O}^{17}\text{O})^+$, extremely faint; and $(^{16}\text{O}^{18}\text{O})^+$, faint. The spectrum would resemble that below.



Problem 2

Hydroxylamine, NH_2OH , is subjected to electron bombardment. The products are passed through a mass spectrograph. The two pairs of lines formed indicate charge/mass ratios of 0.0625, 0.0588 and 0.1250, 0.1176. How can this be interpreted?

Answer

It is always assumed that integral numbers of charges are involved. The dimensions used are electron charges/gram (not coulombs/gram),

hence we can invert these numbers to find for each particle the number of grams per charge.

$$\frac{1}{0.0625} = 16.0 \frac{\text{grams}}{\text{electron charge}}$$

$$\frac{1}{0.0588} = 17.0 \frac{\text{grams}}{\text{electron charge}}$$

$$\frac{1}{0.1250} = 8.00 \frac{\text{grams}}{\text{electron charge}}$$

$$= 16.0 \frac{\text{grams}}{2 \text{ electron charges}}$$

$$\frac{1}{0.1176} = 8.50 \frac{\text{grams}}{\text{electron charge}}$$

$$= 17.0 \frac{\text{grams}}{2 \text{ electron charges}}$$

A particle with mass 16 grams per mole is NH_2 , and a particle with mass 17 grams per mole is OH . Hence the spectrum can be explained in terms of the species NH_2^+ , OH^+ , NH_2^{2+} , and OH^{2+} .

Problem 3

In a nuclear reaction of the type called "nuclear fusion," two nuclei come together to form a larger nucleus. For example, deuterium nuclei, ${}^2_1\text{H}$, and tritium nuclei, ${}^3_1\text{H}$, can "fuse" to form helium nuclei, ${}^4_2\text{He}$, and a neutron:



How many grams of hydrogen would have to be burned (to gaseous water) to liberate the same amount of heat as liberated by fusion of one mole of ${}^2_1\text{H}$ nuclei? Express the answer in tons ($1 \text{ ton} = 9.07 \times 10^5 \text{ g}$).

Answer

One mole of H_2 burned to $\text{H}_2\text{O}(\text{g})$ liberates 57.8 kcal.

$$\frac{4.05 \times 10^7}{57.8} \text{ moles of } \text{H}_2 \text{ burned to } \text{H}_2\text{O}(\text{g}) \text{ liberate}$$

$$4.05 \times 10^7 \text{ kcal.}$$

$$7.01 \times 10^5 \text{ moles of } \text{H}_2 \text{ burned to } \text{H}_2\text{O}(\text{g}) \text{ liberate}$$

$$4.05 \times 10^7 \text{ kcal.}$$

$$(7.01 \times 10^5) \times 2.02 \text{ g/mole} = 1.42 \times 10^6 \text{ g of}$$

$$\text{H}_2 \text{ to liberate } 4.05 \times 10^7 \text{ kcal.}$$

$$\frac{1.42 \times 10^6 \text{ g}}{9.07 \times 10^5 \text{ g/ton}} = 1.57 \text{ tons of } \text{H}_2 \text{ liberate}$$

$4.05 \times 10^7 \text{ kcal}$, the heat liberated by 2.00 grams of deuterium fusing with tritium.

Problem 4

Write equations for the following reactions:

- beta decay of ${}^{253}_{98}\text{Cf}$.
- alpha decay of ${}^{253}_{100}\text{Fm}$.
- the formation of ${}^{120}_{50}\text{Sn}$ by positron emission from an antimony isotope.

Answer

- ${}^{253}_{98}\text{Cf} \longrightarrow {}^{253}_{99}\text{Es} + {}^0_{-1}e$
- ${}^{253}_{100}\text{Fm} \longrightarrow {}^{249}_{98}\text{Cf} + {}^4_2\text{He}$
- ${}^{120}_{51}\text{Sb} \longrightarrow {}^{120}_{50}\text{Sn} + {}^0_{+1}e$

Problem 5

The half-life of ${}^{253}_{100}\text{Fm}$ is 4.5 days. What fraction of a mole of fermium would remain after 13.5 days (three half-lives)?

Answer

Each half-life removes one-half the remaining material. After three half-lives $(\frac{1}{2})^3$ or $\frac{1}{8}$ of the original sample remains. Thus $\frac{1}{8}$ mole remains.

Problem 6

The half-life of ${}^{125}_{53}\text{I}$ is 60 days. What percent of original radioactivity would be present after 360 days?

Answer

In 360 days 6 half-lives would elapse.

$$\text{Fraction remaining is } \left(\frac{1}{2}\right)^6 = \frac{1}{2^6} = \frac{1}{64}$$

$$(\frac{1}{64})(100) = 1.5\% \text{ remaining}$$

Problem 7

The ${}^{14}_6\text{C}$ nuclide undergoes beta decay.

- What stable nuclide is formed?
- Demonstrate the electron balance in the equation.
- The mass difference between reactants and products is $1.66 \times 10^{-4} \text{ g/mole}$. Calculate the total energy in kcal released in this process.

Answer

- ${}^{14}_6\text{C} \longrightarrow {}^{14}_7\text{N} + {}^0_{-1}e$
- ${}^{14}_6\text{C}$ has 6 electrons
 ${}^{14}_7\text{N}$ has 7 electrons

Thus the electrons do not balance unless the nitrogen atom is charged or some electrons are absorbed from the surroundings.

$$\begin{aligned}
 \text{(c) } E &= mc^2 \\
 &= (1.66 \times 10^{-4} \text{ g/mole}) (3 \times 10^{10} \text{ cm/sec})^2 \\
 &\quad \times (2.4 \times 10^{-11} \text{ kcal/erg}) \\
 &= 3.6 \times 10^6 \text{ kcal/mole}
 \end{aligned}$$

The erg to kcal conversion factor (2.4×10^{-11}) is used on Textbook p. 422.

Problem 8

Fission of uranium gives a variety of fission products including praseodymium, Pr. If the process by which praseodymium is formed gives $^{147}_{59}\text{Pr}$ and three neutrons, what is the other nuclear product?

**Answer**

The subscript indicates the number of protons. We begin with 92 (in the uranium nucleus), and 59 are accounted for in the praseodymium nucleus. The remaining protons ($92 - 59 = 33$) are in the other product. Element 33 is arsenic, $_{33}\text{As}$.

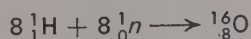
The superscript indicates the total number of nucleons. We begin with $235 + 1 = 236$. Of these, praseodymium accounts for 147, and the three neutrons account for 3 more. The remaining nucleons are in the arsenic nucleus.

$$236 - 147 - 3 = 86$$

The product is the arsenic isotope, $^{86}_{33}\text{As}$.

Problem 9

For $^{16}_8\text{O}$, the mass difference between products and reactants in the equation



is 0.137 g/mole. Calculate the binding energy per nucleon in $^{16}_8\text{O}$ as kcal per mole.

Answer

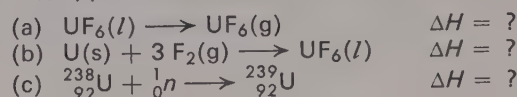
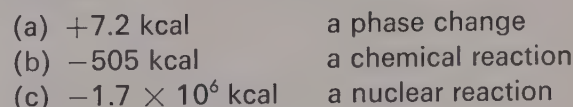
$$\begin{aligned}
 E &= mc^2 \\
 &= (0.137 \text{ g/mole}) (3 \times 10^{10} \text{ cm/sec})^2 \\
 &\quad \times (2.4 \times 10^{-11} \text{ kcal/erg}) \\
 &= 2.96 \times 10^9 \text{ kcal/mole}
 \end{aligned}$$

$^{16}_8\text{O}$ contains 16 nucleons so the binding energy per nucleon is

$$\frac{2.96 \times 10^9}{16} = 1.85 \times 10^8 \text{ kcal per mole of nucleons}$$

Problem 10

Which of the following reactions is most likely to have a heat effect of -505 kcal? Which would be -1.7×10^6 kcal? Which would be $+7.2$ kcal?

**Answer****Problem 11**

A piece of wood recently obtained from a living plant will give carbon having 15.2 ± 0.1 beta particles/min/gram. What age is a sample that gives 3.8 beta particles/min/gram?

Answer

The old sample has $\frac{3.8}{15.2} = 0.25$ or $\frac{1}{4}$ the radioactivity of a fresh carbon sample.

One-fourth of the activity remains after 2 half-lives, which for ^{14}C is

$$2(5570) = 11,140 \text{ years}$$

The uncertainty in 3.8 is 1 part in 38; so the sample age is $11,100 \pm 250$ years.

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CHEM Study films may be obtained by purchase, lease, or subscription from any of the offices of Modern Learning Aids shown below. All films obtained by subscription are guaranteed to be delivered on the confirmed date. For further information, write Modern Learning Aids.

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TL 3-1805

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160 E. Grand Avenue
467-6475

Cincinnati, Ohio 45202
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Garfield 1-2516

Cleveland, Ohio 44115
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NAME	SYMBOL	ATOMIC NUMBER	MOLAR MASS	NAME	SYMBOL	ATOMIC NUMBER	MOLAR MASS
Actinium	Ac	89	(227)	Mercury	Hg	80	200.6
Aluminum	Al	13	27.0	Molybdenum	Mo	42	95.9
Americium	Am	95	(243)	Neodymium	Nd	60	144.2
Antimony	Sb	51	121.8	Neon	Ne	10	20.2
Argon	Ar	18	39.9	Neptunium	Np	93	(237)
Arsenic	As	33	74.9	Nickel	Ni	28	58.7
Astatine	At	85	(210)	Niobium	Nb	41	92.9
Barium	Ba	56	137.3	Nitrogen	N	7	14.01
Berkelium	Bk	97	(247)	Nobelium	No	102	(253)
Beryllium	Be	4	9.01	Osmium	Os	76	190.2
Bismuth	Bi	83	209.0	Oxygen	O	8	16.00
Boron	B	5	10.8	Palladium	Pd	46	106.4
Bromine	Br	35	79.9	Phosphorus	P	15	31.0
Cadmium	Cd	48	112.4	Platinum	Pt	78	195.1
Calcium	Ca	20	40.1	Plutonium	Pu	94	(242)
Californium	Cf	98	(251)	Polonium	Po	84	210
Carbon	C	6	12.01	Potassium	K	19	39.1
Cerium	Ce	58	140.1	Praseodymium	Pr	59	140.9
Cesium	Cs	55	132.9	Promethium	Pm	61	(145)
Chlorine	Cl	17	35.5	Protactinium	Pa	91	(231)
Chromium	Cr	24	52.0	Radium	Ra	88	(226)
Cobalt	Co	27	58.9	Radon	Rn	86	(222)
Copper	Cu	29	63.5	Rhenium	Re	75	186.2
Curium	Cm	96	(248)	Rhodium	Rh	45	102.9
Dysprosium	Dy	66	162.5	Rubidium	Rb	37	85.5
Einsteinium	Es	99	(254)	Ruthenium	Ru	44	101.1
Erbium	Er	68	167.3	Samarium	Sm	62	150.4
Europium	Eu	63	152.0	Scandium	Sc	21	45.0
Fermium	Fm	100	(253)	Selenium	Se	34	79.0
Fluorine	F	9	19.0	Silicon	Si	14	28.1
Francium	Fr	87	(223)	Silver	Ag	47	107.9
Gadolinium	Gd	64	157.2	Sodium	Na	11	23.0
Gallium	Ga	31	69.7	Strontium	Sr	38	87.6
Germanium	Ge	32	72.6	Sulfur	S	16	32.1
Gold	Au	79	197.0	Tantalum	Ta	73	180.9
Hafnium	Hf	72	178.5	Technetium	Tc	43	(99)
Helium	He	2	4.00	Tellurium	Te	52	127.6
Holmium	Ho	67	164.9	Terbium	Tb	65	158.9
Hydrogen	H	1	1.008	Thallium	Tl	81	204.4
Indium	In	49	114.8	Thorium	Th	90	232.0
Iodine	I	53	126.9	Thulium	Tm	69	168.9
Iridium	Ir	77	192.2	Tin	Sn	50	118.7
Iron	Fe	26	55.8	Titanium	Ti	22	47.9
Krypton	Kr	36	83.8	Tungsten	W	74	183.9
Lanthanum	La	57	138.9	Uranium	U	92	238.0
Lawrencium	Lw	103	(259)	Vanadium	V	23	50.9
Lead	Pb	82	207.2	Xenon	Xe	54	131.3
Lithium	Li	3	6.94	Ytterbium	Yb	70	173.0
Lutetium	Lu	71	175.0	Yttrium	Y	39	88.9
Magnesium	Mg	12	24.3	Zinc	Zn	30	65.4
Manganese	Mn	25	54.9	Zirconium	Zr	40	91.2
Mendelevium	Md	101	(256)	(unnamed)*	?	104	(260)

* Discovery reported in 1964.

Molar masses based on $^{12}\text{C} + 12.000$.

Numbers in parentheses give the mass number of the most stable isotope.

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